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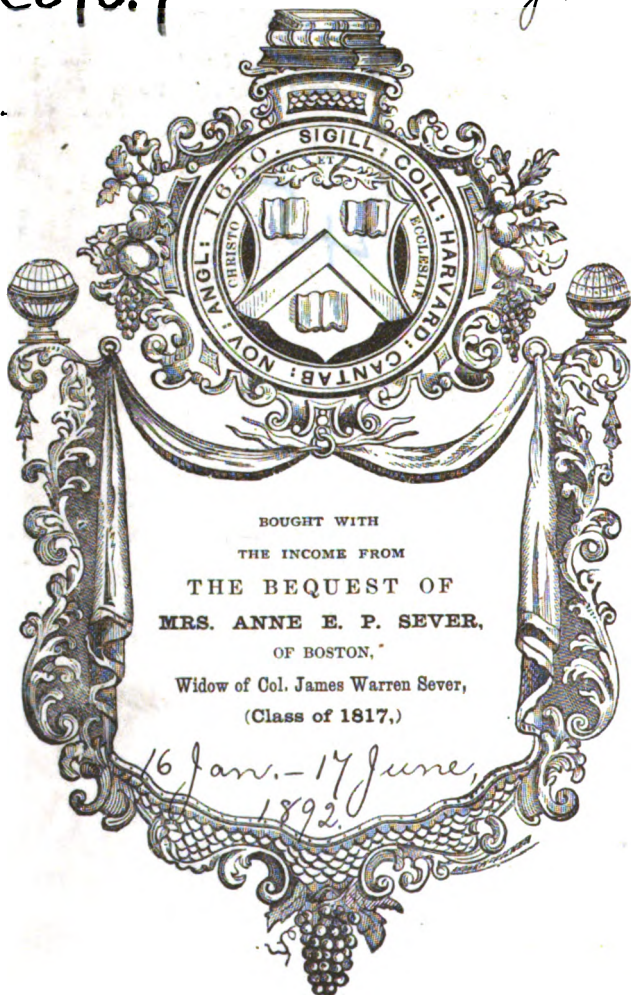
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LORD KELVIN, LL.D. P.R.S. &c.  
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AND  
WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

---

“Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes.” JUST. LIPS. *Poët. lib. i. cap. 1. Not.*

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JANUARY—JUNE 1892.

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"Meditationis est perscrutari occulta; contemplationis est admirari  
perspicua . . . . Admiratio generat quæstionem, quæstio investigationem,  
investigatio inventionem."—*Hugo de S. Victore.*

---

—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condat,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



# CONTENTS OF VOL. XXXIII.

(FIFTH SERIES).

NUMBER CC.—JANUARY 1892.

	Page
Lord Rayleigh on Reflexion from Liquid Surfaces in the Neighbourhood of the Polarizing Angle .....	1
Messrs. E. L. Nichols and B. W. Snow on the Character of the Light emitted by Incandescent Zinc Oxide.....	19
Dr. G. Gore on a Method of Measuring Loss of Energy due to Chemical Union &c.....	28
Dr. J. W. L. Glaisher on the Connexion between Recurring Formulæ involving Sums of Divisors and the Corresponding Formulæ involving Differences between Sums of Even and Uneven Divisors .....	54
Prof. A. Gray on the Calculation of the Induction-Coefficients of Coils, and the Construction of Standards of Inductance, and on Absolute Electrodynamometers .....	62
Mr. J. Larmor on the Influence of Flaws and Air-cavities on the Strength of Materials .....	70
Mr. B. A. Lehfeldt on a Galvanometric Method of Measuring H .....	78
Mr. J. Brown on the Theory of Electrolytic Conduction of Clausius; and on some recent Evidence for the Dissociation Theory of Electrolysis .....	82
Mr. H. Crew on a New Method for obtaining a Constant Temperature .....	89
Mr. A. P. Laurie on the Existence of a Compound of Gold and Tin .....	94
Prof. D. Mendeléef on the Variation in the Density of Water with the Temperature .....	99
Mr. S. U. Pickering on the Densities of Sulphuric-Acid Solutions .....	132
Notices respecting New Books:—	
Prof. Ostwald's 'Solutions;' being the Fourth Part of a Text-Book of General Chemistry .....	144
Dr. Watts's Index of Spectra, Appendix B .....	147
Mr. Gore's Star Groups .....	147
Dr. Williamson's Elementary Treatise on the Integral Calculus .....	148
Dr. Besant's Solutions of Examples in Conic Sections, treated Geometrically .....	149

	Page
Proceedings of the Geological Society :—	
Mr. T. F. Jamieson's Supplementary Remarks on Glen Boy .....	149
Prof. E. Hull's Comparison of the Red Rocks of the South Devon Coast with those of the Midland and Western Counties.....	151
Rev. A. Irving's Supplementary Note to the Paper on the 'Red Rocks of the Devon Coast-section,' Q. J. G. S. 1888 .....	151
On the Concordance of Orthobaric Curves for Solutions and Homogeneous Liquids, by L. Natanson .....	152

### NUMBER CCI.—FEBRUARY.

Prof. S. Young on the Generalizations of Van der Waals regarding "Corresponding" Temperatures, Pressures, and Volumes. (Plates I.-III.) .....	153
Prof. W. E. Ayrton and Mr. T. Mather on the Construction of Non-Inductive Resistances. (Plate IV.) .....	186
Dr. C. V. Burton on a Theory concerning the Constitution of Matter .....	191
Prof. A. W. Rücker on the Density and Composition of Dilute Sulphuric Acid.—No. II. ....	204
Lord Rayleigh on the Theory of Surface Forces.—II. Com- pressible Fluids.....	209
Mr. H. L. Callendar on some Experiments with a Platinum Pyrometer on the Melting-points of Gold and Silver. (Plate V.) .....	220
Notices respecting New Books :—	
Mr. J. Parker's Elementary Thermodynamics .....	228
Clerk Maxwell's Theory of Heat, Tenth Edition edited by Lord Rayleigh .....	231
On a Consequence of the Poisson-Mossotti Theory, by Gottlieb Adler .....	233
On the Electromotive Force of Gas-batteries, by Gertscho Markovsky .....	235
Velocity of Sound in Membranous Bodies, by F. Melde ....	236
The Solitary Wave: Correction of a Sign .....	236

NUMBER CCII.—MARCH.

	Page
Prof. T. G. Bonney's Petrological Notes on the Euphotide or Saussurite-smaragdite Gabbro of the Saasthal .....	237
Mr. J. McCowan on the Theory of Long Waves and its Application to the Tidal Phenomena of Rivers and Estuaries.	250
Mr. J. Walker on the Intensity at the Focal Point of a Telescope, when the Object-glass is covered by a Diaphragm pierced with Circular Apertures .....	266
Prof. J. Perry on Struts and Tie-Rods with Lateral Loads ..	269
Mr. S. U. Pickering on the Hypothetical Tetrachloride of Manganese.....	284
Sir W. Thomson on the Kinetic Theory of the Dissipation of Energy .....	291
Messrs. W. Lucas and T. A. Garrett on a Detector for Spark in Hertz's Resonator .....	299
Prof. L. Natanson's Dynamical Illustration of the Isothermal Formula.....	301
Mr. W. Hibbert on a Permanent Magnetic Field .....	307
Notices respecting New Books :—	
Mr. J. F. Blake's Annals of British Geology, 1890 ....	314
On the Refraction of Sound, and its Velocity in Porous Substances permeable to Sound, by N. Hessehus .....	316

NUMBER CCIII.—APRIL.

Dr. T. Ewan on the Absorption-Spectra of some Copper Salts in Aqueous Solution .....	317
Dr. G. Gore on Chemical Equilibrium in Mixed Electrolytes..	342
Prof. A. Anderson on the Resistance and Self-Induction of Branched Circuits.....	352
Lord Rayleigh on Maxwell's Investigation respecting Boltzmann's Theorem .....	356
Mr. C. Tomlinson on an Experiment Illustrative of the Formation of Rocking Stones .....	359
Lord Rayleigh's Experiments upon Surface-Films.....	363
Mr. John Trowbridge on Wave Propagation of Magnetism ..	374
Messrs. E. L. Nichols and B. W. Snow on the Selective Absorption of Light by Optical Glass and Calc-spar .....	379
Notices respecting New Books :—	
F. Karrer's Guide through the Collection of Building-materials in the Imperial Natural-history Museum at Vienna .....	382
Mr. A. M. Worthington's Dynamics of Rotation .....	383

	Page
Proceedings of the Geological Society :—	
Rev. J. F. Blake on the Rocks mapped as Cambrian in Caernarvonshire .....	384
Mr. W. Shone on the Subterranean Denudation of the Glacial Drift, a probable cause of Submerged Peat and Forest-beds .....	384
Mr. A. C. Nicholson on High Level-Glacial Gravels, Gloppa, Cynr-y-bwch, near Oswestry .....	385
Mr. H. W. Monckton on the Gravels on the South of the Thames from Guildford to Newbury; and on the Bagshot Beds of Bagshot Heath .....	385
Mr. A. J. Jukes-Browne and Prof. J. B. Harrison on the Geology of Barbados .....	386
On the Intensity of the Radiation of Gas under the Influence of the Electrical Discharge: preliminary notice by K. Angström .....	387
On the Repulsive Force of Radiating Bodies, by Peter Lebedew .....	391
An Electrolytic Experiment, by Leo Arons .....	395
On a Method of Determining Electromagnetic Radiation, by Prof. Klemencič .....	396

---

#### NUMBER CCIV.—MAY.

Mr. R. C. Nichols on the Resistances to Transverse Strain in Beams .....	397
Mr. M. F. FitzGerald on the Flexure of Long Pillars under their own Weight .....	428
Mr. C. Barus on the Change of Heat Conductivity on passing isothermally from Solid to Liquid .....	431
Prof. J. Perry on Choking Coils .....	433
Mr. S. U. Pickering on the Recognition of Changes of Curvature by Means of a Flexible Lath .....	436
Lord Kelvin on a Decisive Test-case disproving the Maxwell-Boltzmann Doctrine regarding Distribution of Kinetic Energy .....	466
Lord Rayleigh on the Theory of Surface Forces.—III. Effect of Slight Contaminations .....	468
Mr. R. E. Hughes on some Properties of Dried Hydrogen Sulphide Gas .....	471
Notices respecting New Books :—	
Dr. Watts's Index of Spectra, Appendix C. ....	475
On the Influence of Pressure on the Viscosity of Liquids, by R. Cohen .....	476

---



## NUMBER CCV.—JUNE.

	Page
Mr. A. M'Aulay on Quaternions as a practical Instrument of Physical Research.....	477
Mr. W. Baily on the Construction of a Colour Map. (Plate VIII.) .....	496
Dr. G. J. Stoney on an Analysis of the Spectrum of Sodium, including an Inquiry into the true place of the Lines that have been regarded as Satellites. (Plates VI. & VII.)....	503
Prof. E. F. Herroun on the Electromotive Forces of Gold and of Platinum Cells .....	516
Dr. C. Ludeking on the Action of the Electric Discharge on Gases and Vapours .....	521
Dr. F. T. Trouton and Mr. W. E. Lilly on a Method for determining the Specific Inductive Capacity of Dielectrics ....	529
Mr. J. Brown on the Difference of Potential at the Contact of Mutually Reacting Liquids .....	532
Proceedings of the Geological Society :—	
Rev. E. Hill and Prof. T. G. Bonney on the Hornblende-schists, Gneisses, and other Crystalline Rocks of Sark	539
Messrs. J. R. Dakyns and J. J. H. Teall on the Plutonic Rocks of Garabal Hill and Meall Breac .....	540
On the Value of the Brightness of Spectral Colours with different absolute Intensity, by A. König and R. Ritter ..	541
On the Glow-Discharge, by E. Warburg .....	543
Prize for Researches in Physics, offered by Schnyder von Wartensee's Foundation for Science and Art, Zürich ....	544
Index .....	545

## PLATES.

- I.-III. Illustrative of Prof. S. Young's Paper on the Generalizations of Van der Waals regarding "Corresponding" Temperatures, Pressures, and Volumes.
- IV. Illustrative of Prof. W. E. Ayrton and Mr. T. Mather's Paper on the Construction of Non-Inductive Resistances.
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[FIFTH SERIES.]

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JANUARY 1892.

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- I. *On Reflexion from Liquid Surfaces in the Neighbourhood of the Polarizing Angle.* By Lord RAYLEIGH, Sec. R.S.\*

BY the experiments of Jamin and others it has been abundantly proved that in the neighbourhood of the polarizing angle the reflexion of light from ordinary transparent liquids and solids deviates sensibly from the laws of Fresnel, according to which the reflexion of light polarized perpendicularly to the plane of incidence should vanish when the incidence takes place at the Brewsterian angle. It is found, on the contrary, that in most cases the residual light is sensible at all angles, and that the change of phase by  $180^\circ$ , which, according to Fresnel's formula, should occur suddenly, in reality enters by degrees, so that in general plane-polarized light acquires after reflexion a certain amount of ellipticity. Although Jamin describes the non-evanescence at the polarizing angle and the ellipticity in its neighbourhood as "*deux ordres de phénomènes de nature différente*," it is clear that they are really inseparable parts of one phenomenon. If we suppose the incident light polarized perpendicularly to the plane of incidence to be given, the vibration which determines the reflected light at various angles may be represented in amplitude and phase by the situation of points relatively to an origin and coordinate axes. Thus, according to Fresnel's formula, the locus of these points is the axis of abscissæ  $XX'$

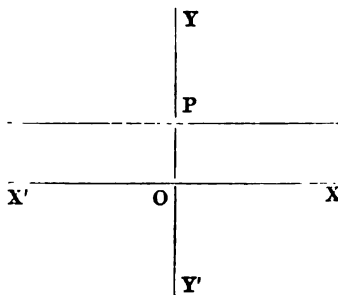
\* Communicated by the Author.

*Phil. Mag.* S. 5. Vol. 33. No. 200. Jan. 1892.

B

## 2 Lord Rayleigh on Reflexion from Liquid Surfaces

itself, the point  $O$  corresponding to the polarizing angle, at which the reflexion vanishes, and in passing which there is a sudden change of phase of  $180^\circ$ . If the reflexion remains finite at all angles, the curve in question meets the axis  $Y Y'$  at some point  $P$ , not coincident with  $O$ , and the corresponding phase differs by a quarter-period from the phases met



with at a distance from this angle. So far as experiment can yet show, this curve may be a straight line parallel to  $XX'$ , and at a short distance from it. If it lie above  $XX'$  the reflexion is what Jamin characterizes as positive; if below, the reflexion is negative.

To this order of approximation the behaviour of a transparent body reflecting light of given wave-length is determined by two constants, (1) the refractive index  $\mu$ , and (2) the intensity of reflexion at the angle  $\tan^{-1}\mu$  when the light is polarized perpendicularly to the plane of incidence. The most convenient form of the second constant for experimental purposes is the ratio of reflected amplitudes for the two principal planes when the light, incident at the angle  $\tan^{-1}\mu$ , is polarized at  $45^\circ$  to these planes. It may be called the ellipticity, and, after Jamin, will be denoted by  $k$ . According to Fresnel  $k=0$ ; but Jamin found for water  $k=-0.0577$ , and for absolute alcohol  $k=+0.0208$ . Contrasting liquids with solids, he remarks\*, "on vient de voir que leur polarisation est elliptique, et qu'il est impossible d'en trouver la cause dans une constitution moléculaire anormale." And, again:—"Il est jusqu'à présent impossible de constater une relation simple entre la valeur du coefficient  $k$  et l'indice de réfraction; tout porte à croire, au contraire, que ces deux constantes sont indépendantes, l'une de l'autre. Mais, à défaut de loi pré-

\* "Mémoire sur la réflexion de la Lumière à la surface des Liquides." *Ann. Chim.* xxxi. p. 165 (1851).

cise, on peut remarquer une tendance du coefficient  $k$  à diminuer avec l'indice, et quand celui-ci est approximativement égal à 1.45,  $k$  est nul : l'indice continuant à décroître, le coefficient  $k$  reprend des valeurs sensibles et croissantes."

Since the time of Jamin many valuable observations upon reflexion have been made by Quincke and others, which it is not necessary for my purpose further to refer to. In 1889\* Drude made the very important observation that the ellipticity of a freshly split surface of rock-salt is very small, but that it rapidly increases on standing. And he concludes generally that solid bodies reflect from natural cleavage surfaces according to the laws of Fresnel. It is remarkable that fluids are excluded from this statement. Indeed Drude expressly remarks that in fluids the natural surface-sheet, which forms the transition from one medium to another, exercises an essential influence upon the reflexion.

Nearly contemporaneously with Drude's observation I made a first attempt to examine whether the different behaviour which Plateau found for water and for alcohol in respect of superficial viscosity, and which I was disposed to attribute to surface contamination, corresponded to anything in the phenomena of reflexion near the polarizing angle, but at that time I was misled by a faulty nicol, and failed to observe anything distinctive. Subsequently, having proved that the superficial viscosity of water was due to a greasy contamination, whose thickness might be much less than one millionth of a millimetre, I too hastily concluded that films of such extraordinary tenuity were unlikely to be of optical importance, until, prompted by a remark of Sir G. Stokes, I made an actual estimate of the effect to be expected. The thickness required to stop camphor movements, viz.,  $2 \times 10^{-7}$  centim., is about  $\frac{1}{300}$  of  $\lambda$ . This will be one factor in the expression for the amplitude of reflexion due to grease. There will be another somewhat small factor expressive of the difference of optical quality between grease and water ; so that the intensity of reflexion at the polarizing angle might on this view be of the order  $10^{-6}$ , or  $10^{-7}$ , a quantity quite appreciable, when the incident light is from the sun. Thus encouraged, I returned to the attack, and on October 2nd, 1890, examined the image of the sun as reflected from water at the polarizing angle. The arrangements were very simple. Sunlight reflected horizontally into the dark room from a heliostat outside was again reflected downwards by an adjustable mirror. The water was contained in a large porcelain dish to the

\* Wied. Ann. xxxvi. p. 532.

#### 4 Lord Rayleigh on Reflexion from Liquid Surfaces

depth of about an inch, and at the bottom of the dish was placed a piece of darkly-coloured glass, not quite horizontal, with the view of annulling the diffuse reflexion. The reflected image was observed with a nicol, from which the glass covering disks had been removed, simply held in the hand. The appearance of the dark spot, brought to the centre of the sun's disk, was at once recognized to be dependent upon the condition of the water-surface. When the surface was clean, the spot was dark and its width (in the plane of incidence) was about  $\frac{1}{3}$  or  $\frac{1}{4}$  of the solar diameter. Moreover there was a strong appearance of colour, brown above and blue below, evidently due to the dependence of the polarizing angle upon the wave-length of the light. But when the surface was greasy, *even although camphor fragments still rotated briskly*, the band lost its darkness, became diffuse, and showed but little colour. When the greasy film was about sufficient to stop the camphor movements, the contrast with the effect of clean water was very marked\*.

The surface was cleansed by the aid of the expansible hoop employed in my former experiments. This is made of very thin sheet brass, about 2 inches wide. It is placed upon the water, already reasonably clean, in its contracted condition, so that the area enclosed is but small. When it is opened out, say to a circle of about 10 inches diameter, the internal surface of the water is rendered more clean, and the external less clean, than before. To get the best result it is desirable to go through the operation of expanding two or three times, probably because the cleaned water-surface acquires grease from the internal surface of the brass hoop. It will be evident that the action depends upon the hoop not being completely wetted†. Otherwise the grease could repass from the outside back into the interior. For this reason the hoop cannot be expected to succeed with liquids like alcohol.

By taking advantage of the apparent motion of the sun in altitude, these observations may be repeated in summer without any heliostat, or reflexion, other than that of the water itself. Thus on June 26 the dish was placed on a table below the window of an undarkened room, and the passage of the spot across the sun's disk was watched. The spot was central at about 4<sup>h</sup> 0<sup>m</sup>, and the instant of centrality could be determined to within 10°, and probably to within 5°. On August 15, when the sun's motion in altitude was slower,

\* Phil. Mag. November 1890, p. 400.

† Since imperfect wetting must be attributed to residual grease, it would appear that the operation of the hoop is incomplete at best. Nevertheless, it is a very useful and convenient appliance.



centrality occurred at about  $3^h 10^m$ , and the precise instant was less well determined.

To see the band at its best requires an unusually good nicol. Whether on account of residual defects in the nicols, or in the lenses of my eyes, vision was improved by the use of a horizontal slit, about  $\frac{1}{8}$  inch wide, cut out of black paper, and attached to the cork mounting of the nicol on the side next the eye. Under these conditions the band seen from clean water looks black and well defined, and of width amounting to  $\frac{1}{4}$  or  $\frac{1}{5}$  of the solar diameter. A still further improvement sometimes attends the use of a second nicol, held parallel to the first, through which the light passes before reflexion from the water. With these arrangements the band is visibly deteriorated by quantities of grease far less than is required to check the camphor movements.

It has been mentioned that the dark band from clean water was fairly narrow; and it will be of interest to inquire what is to be expected upon the assumption that Fresnel's formulæ really express the facts of the case. We will write

$$S = \frac{\sin(\theta - \theta_1)}{\sin(\theta + \theta_1)}, \quad T = \frac{\tan(\theta - \theta_1)}{\tan(\theta + \theta_1)}, \quad \dots \quad (1)$$

so that the ratio of amplitudes of the two polarized components, corresponding to a primitive polarization at  $45^\circ$ , is

$$T/S = \frac{\cos(\theta + \theta_1)}{\cos(\theta - \theta_1)}, \quad \dots \quad (2)$$

vanishing when  $\theta + \theta_1 = \frac{1}{2}\pi$ , that is when  $\theta = \tan^{-1}\mu$ . We will suppose that the angle of incidence has approximately this value, and write  $\theta + \delta\theta$ ,  $\theta_1 + \delta\theta_1$  for  $\theta$ ,  $\theta_1$  respectively. Thus in the neighbourhood of the polarizing angle the ratio is

$$- \frac{\delta\theta + \delta\theta_1}{\cos(\theta - \theta_1)}$$

approximately.

Now

$$\sin\theta = \mu \sin\theta_1, \quad \cos\theta \delta\theta = \mu \cos\theta_1 \delta\theta_1,$$

so that

$$\delta\theta_1 = \frac{\cos\theta \delta\theta}{\mu \cos\theta_1} = \frac{\sin\theta_1 \delta\theta}{\mu \sin\theta} = \frac{\delta\theta}{\mu^2}.$$

Hence

$$T/S = - \frac{(\mu^2 + 1) \delta\theta}{\mu^2 \cos^2(\theta - \theta_1)}, \quad \dots \quad (3)$$

For water

$$\mu_0 = 1.3336, \quad \theta = \tan^{-1} \mu = 53^\circ 8', \quad \theta_1 = 36^\circ 52';$$

and

$$T/S = 1.627 \delta\theta, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$T^2/S^2 = 2.649 (\delta\theta)^2. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Let us calculate the ratio corresponding to the upper or lower limb of the sun when the spot is central; that is, let  $\delta\theta$  be the angular radius of the sun, whose value in minutes is 16. Thus

$$\delta\theta = \frac{16\pi}{10800},$$

and corresponding thereto from (5)

$$T^2/S^2 = 5.74 \times 10^{-5}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The width of the band actually observed had been estimated at about  $\frac{1}{2}$  of the solar diameter, so that at its limits

$$T^2/S^2 = 2 \times 10^{-6}.$$

The band was thus about as narrow as Fresnel's formulæ would lead one to expect, and its deterioration by a film of grease might be anticipated as at least probable from the rough estimate above given of the effect of such a film.

The results so far obtained were already sufficient to show that Jamin's value of  $k$ , viz.  $-.00577$ , must be (numerically) much in excess of the truth. For according to it, since  $k^2 = 3.33 \times 10^{-5}$ , the minimum illumination at the centre of the spot should be half as great as Fresnel's formulæ make it at the limb of the sun, so that the whole diameter of the sun would be almost equally obscured. The observed narrowness of the band, even in the absence of all precise measures, thus constitutes a proof that Jamin's  $k$  is several times too great, and suffices to render it almost certain that the water-surface with which he worked was highly contaminated.

It has already been mentioned that a well-formed band was attended with a marked appearance of colour. The account of this rendered by Fresnel's formulæ is quite satisfactory. Let us calculate the illumination at the centre of the band corresponding to  $\mu$ , due to a change from  $\mu$  to  $\mu + \delta\mu$ , comparing it, as usual, with  $S^2$ . In the differentiation  $\theta$  is to be treated as constant, and the change in  $\theta_1$ , viz.  $\delta\theta_1$ , is due to  $\delta\mu$ . From (2),

$$T/S = \frac{\cos(\frac{1}{2}\pi + \delta\theta_1)}{\cos(\theta - \theta_1 - \delta\theta_1)} = \frac{-\delta\theta_1}{\cos(\theta - \theta_1)};$$

and the relation between  $\delta\theta_1$  and  $\delta\mu$  is

$$\cos \theta_1 \delta\theta_1 = - \frac{\sin \theta \delta\mu}{\mu^2},$$

or

$$\delta\theta_1 = -\delta\mu/\mu^2,$$

since  $\cos \theta_1 = \sin \theta$ . Thus

$$T/S = \frac{\delta\mu}{\mu^2 \cos(\theta - \theta_1)} \cdot \cdot \cdot \cdot (7)$$

In the case of water,

$$\mu_G = 1.341, \quad \mu_B = 1.331, \quad \delta\mu = .010.$$

From these data,

$$T^2/S^2 = 3.46 \times 10^{-5};$$

showing that if the spot is central for Fraunhofer's line B, the illumination at the centre for G is more than half as great as is found (6) for B at the upper and lower limbs of the sun. A considerable development of colour is thus to be expected, when the band is well formed.

The band may be achromatized with the aid of a suitable prism, held between the nicol and the eye, but of course at the expense of introducing colour at the upper and lower limbs of the sun. I had at my disposal a glass prism of  $10^\circ$ . This diminished, but could not annul, the colour when held nearly in the position of minimum deviation; but by sufficient sloping the band was practically achromatized. When more dispersive materials, *e. g.* benzole or bisulphide of carbon, were substituted for water, the development of colour is very great, and in the case of the latter made it impossible to judge of the perfection of the band. The above-mentioned glass prism was of course quite insufficient for compensation.

The magnitude of these chromatic effects is given at once by Brewster's law, which we may write in the form

$$\tan(\theta + \delta\theta) = \mu + \delta\mu.$$

Thus

$$\delta\theta = \cos^2 \theta \delta\mu = \frac{\delta\mu}{1 + \mu^2}, \quad \cdot \cdot \cdot \cdot (8)$$

which gives the angular displacement of the centre of the dark band, due to the change from  $\mu$  to  $\mu + \delta\mu$ . Let us inquire what small angle (*i*) must be given to a prism of the same material in order that it may be capable of compensating the colour. The deviation D is equal to  $(\mu - 1)i$ , so that  $\delta D = \delta\mu \cdot i$ . Hence, if  $\delta D = \delta\theta$ ,

$$i = \frac{1}{1 + \mu^2} \cdot \cdot \cdot \cdot (9)$$

## 8 Lord Rayleigh on Reflexion from Liquid Surfaces

The necessary angle is thus independent of the dispersive power, and does not vary rapidly with the refractive power, of the substance. For water,  $i=9/25$  in circular measure, or about  $22^\circ$ . For glass ( $\mu=1.5$ ) we should have  $i=18^\circ$ .

An attempt was made to achromatize the band from bisulphide of carbon with a  $15^\circ$  prism of that material. So far as could be judged the colour was compensated, but the observation was imperfect on account of the insufficient angular magnitude of the solar disk.

These experiments on the achromatization of the band had been made in the hope of thereby reducing its apparent width, seeing that according to (8) the difference of position for the lines B and G amounts, in the case of water, to  $13'$ , much more than the apparent width of the band. But the width of the achromatized band could not be set at much less than  $\frac{1}{3}$  of the sun's diameter\*. It seems that in estimating the dimensions of the uncorrected band the eye instinctively allows for the influence of colour.

In experimenting upon water various kinds were tried. Usually the tap-water (from an open cistern) behaved after expansion as well as did distilled water. The brass hoop, judiciously applied, appears to be capable of removing ordinary surface-contamination; but the appearance of the band is liable to be deteriorated by suspended matter, which detracts from the central darkness. So far as could be judged by this method of observation, the best bands were sensibly perfect. There was no evidence of any departure from the law of Fresnel.

Similar results were obtained from other liquids, *e. g.* strong alcohol, sulphuric acid, benzole. Special interest attached to an observation upon a saturated solution of camphor, of which the superficial tension is much lower ( $.72$ ) than that of pure water. The band was sensibly perfect.

Oleate of soda ( $\frac{1}{40}$ ) was troublesome on account of the difficulty of avoiding scum. A pretty good band could be obtained, certainly inferior to the best, possibly owing to residual scum, but much better than from water greased with olive-oil to the point at which the camphor motions are just stopped.

The results last recorded prove that the optical effect is not determined by surface-tension, for the tension of the oleate solution is much less than that of any merely greased surface. A similar conclusion was suggested by the observed difference

\* A coloured glass is still less effective than the compensating prism. A reduction in the intensity of the light necessarily broadens the band. A similar effect occurs if the sun is not quite clear.

of behaviour of various parts of the same surface. A surface, originally clean, and then greased with olive-oil carried upon a previously ignited platinum wire, frequently showed streakiness, when the eye, observing through the nicol, as usual, was focused upon the surface.

Except perhaps in the case of oleate, none of these experiments, many times repeated, gave any evidence of a real departure of properly skimmed surfaces from the laws of Fresnel; and it looked very much as if all the results enunciated for liquids by Jamin were vitiated by the presence of greasy films. That a film of extreme tenuity would suffice was certain. The band from water was very obviously deteriorated by a film of olive-oil, which needed to be condensed four or five times in order to stop the camphor movements.

But it was impossible to rest here. It was necessary actually to measure, or, if that were not possible, to find limits for, the ellipticity of the various surfaces. And for this purpose a much more elaborate apparatus had to be installed.

Sunlight, reflected horizontally from the heliostat, passed through a diaphragm in the shutter of about  $\frac{1}{4}$  inch diameter, and thence to a collimating lens of 23 inches focus. It was next reflected in the required oblique direction by an adjustable mirror, and caused to traverse the polarizing nicol, mounted in a circle that allowed the orientation of the nicol to be read to a minute of angle. After reflexion from the surface under examination the light traversed in succession a quarter-wave-plate and the analysing nicol, and was then received into the eye, either directly, or with the intervention of a small telescope magnifying about twice. In either case the eye was focused upon the diaphragm, which was provided with cross wires; so that the rays which fell upon any part of the retina constituted a parallel pencil, not only at the surface of the liquid, but also in their passage through the nicols and quarter-wave-plate. The latter was of mica, and both it and the analysing nicol were mounted so as to be capable of rotation about the direction of the reflected ray.

The adjustments were made as follows. The analyser and quarter-wave-plate being removed, the mirror and polarizer were adjusted until the dark spot was central in relation to the cross wires. A rotation of the mirror, altering the angle of incidence, moves the spot vertically, while a rotation of the polarizer moves it horizontally. The zero for the eye-nicol could have been found by rotating the polarizer and then recovering the dark spot; but in order to avoid risks of displacement, which might be fatal in such a delicate inquiry, I preferred to leave the first nicol untouched, and to depolarize

the light by the introduction of a parallel plate of quartz. With the aid of this the analysing nicol could be set, and then the mica. If, with the quartz plate in action, the spot is dark and central, all is well adjusted. On removal of the quartz, the band is now seen in full perfection.

One of the difficulties in these experiments lay in the extreme sensitiveness of the liquid surfaces to tremor, a sensitiveness aggravated by the perfect cleanliness required. It had been thought that it would suffice to mount the apparatus upon a shelf attached to the walls of the building, and isolated from the floor. But it appeared that the slightest touch upon the tangent-screw of the divided circle, such as it is necessary to make at the moment of observation, entailed a most distracting tremor. A remedy was found in suspending the dish containing the liquid under examination independently from the roof.

The work has been greatly retarded by want of sunshine. In order to be more independent, I tried to work at the Royal Institution by the electric light. But it appeared impossible to make any observations of value on account of the tremor by which London is pervaded. Moreover the arc-light is very inferior to sunshine for such a purpose.

The theory of the experiment is as follows. According to Fresnel's formulæ the ratios of the reflected to the incident vibrations are, for the two planes of polarization, T and S; in which the reality of T and S indicates that there is no change of phase in reflexion (other than  $180^\circ$ ). The ellipticity is represented by the addition to T of  $iM$ , where  $M$  is small and  $i = \sqrt{-1}$ . Thus if the incident light be polarized in the plane making an angle  $\alpha$  with the principal planes, the reflected vibrations may be represented by

$$(T + iM) \cos \alpha, \quad S \sin \alpha.$$

By the action of the mica, or other compensator, a relative change of phase  $\gamma$  is introduced. This is represented by writing for  $S \sin \alpha$ ,

$$S \sin \alpha (\cos \gamma + i \sin \gamma).$$

Thus the vibration transmitted by the analyser, set at angle  $\beta$ , is

$$\cos \alpha \cos \beta (T + iM) + S \sin \alpha \sin \beta (\cos \gamma + i \sin \gamma);$$

and the intensity of this is

$$(T \cos \alpha \cos \beta + S \sin \alpha \sin \beta \cos \gamma)^2 \\ + (M \cos \alpha \cos \beta + S \sin \alpha \sin \beta \sin \gamma)^2. \quad (10)$$

In order that the light may vanish we must have both

$$T + S \tan \alpha \tan \beta \cos \gamma = 0, \quad . \quad . \quad . \quad (11)$$

$$M + S \tan \alpha \tan \beta \sin \gamma = 0. \quad . \quad . \quad . \quad (12)$$

In the neighbourhood of the polarizing angle,  $M, S$  vary slowly, but  $T$  varies rapidly. Hence, if  $\gamma$  be given, we may regard (12) as determining  $\tan \alpha \tan \beta$ , while (11) gives  $T$ , and thence the precise angle of reflexion for the dark spot. If there be no ellipticity,  $M=0$ ; whence  $\tan \alpha \tan \beta=0$ ,  $T=0$ , indicating, as was to be expected, that the dark spot occurs at the Brewsterian angle.

But this law is not universal. For if there be no compensator,  $\gamma=0$ , and we have as the expression for the intensity,

$$(T \cos \alpha \cos \beta + S \sin \alpha \sin \beta)^2 + M^2 \cos^2 \alpha \cos^2 \beta.$$

Hence, if  $\alpha$  and  $\beta$  are small, the second term cannot be made to vanish, and the brightness is a minimum when

$$T = -S \tan \alpha \tan \beta.$$

The position of the nearly dark spot is thus dependent upon  $\alpha, \beta$ , and assumes the Brewsterian position only when either  $\alpha$  or  $\beta$  vanishes.

In the case of a quarter-wave-plate,  $\gamma = \pm \frac{1}{2}\pi$ , and the equations become

$$T=0, \quad k = \tan \alpha \tan \beta = \mp M/S. \quad . \quad . \quad . \quad (13)$$

The dark spot thus occurs at the Brewsterian angle, while  $\tan \alpha \tan \beta$  gives the value of  $M/S$ , viz. the  $k$  of Jamin. Accordingly if  $\beta$  be set to any convenient angle\*, and  $f$  be then adjusted so as to bring the dark spot to the central position, the product of the tangents of  $\alpha$  and  $\beta$ , each measured from the zeros obtained in the preliminary adjustments, gives  $k$ .

But the following procedure not only affords greater delicacy, but makes us comparatively independent of the positions of the zeros. Set  $\beta$ , e. g., to  $+30^\circ$ , and find  $\alpha$ ; then reset  $\beta$  to  $-30^\circ$ . The new value of  $\alpha$  would coincide with the old one if there were no ellipticity; and the difference of values measures  $\alpha$  upon a doubled scale. If  $\alpha'$  be the second value, so that the difference is  $\alpha' - \alpha$ , then

$$k = \tan 30^\circ \tan \frac{1}{2}(\alpha' - \alpha),$$

\* In my apparatus it was convenient to throw the fine adjustment upon  $\alpha$ .

or as would suffice for all the purposes of the present investigation

$$k = \frac{1}{2} \tan 30^\circ (\alpha' - \alpha). \quad (14)$$

In practice several readings for  $\alpha$  would be taken as quickly as possible,  $\beta$  being reversed between each. In this way there is the best chance of distinguishing casual errors of observation from the results of progressive changes in the condition of the surface under examination. For greater security against error due to maladjustments, readings were often taken in all four positions, differing from one another by  $90^\circ$ , of the quarter-wave mica. The observed differences of  $\alpha$  should be reversed in adjacent positions of the mica, and should be identical in the opposite positions, obtained from one another by rotation through  $180^\circ$ .

In the above reasoning  $\gamma$  has been regarded as independent of  $\lambda$ , but this is of course only roughly true. If we neglect the dispersion of the mica, we may take  $\gamma = \gamma_0 + \delta\gamma$ , where  $\gamma_0$  relates to the mean ray  $\lambda_0$ , while

$$\delta\gamma/\gamma_0 = -\delta\lambda/\lambda_0. \quad (15)$$

If the mica be suitably chosen,  $\gamma_0 = \pm \frac{1}{2}\pi$ .

On this principle of the variability of  $\gamma$  may be explained an effect which was puzzling when first observed. When the water-surface was rather highly contaminated, it was found that the appearance of the spot varied according to the choice of positions for the mica. In one position and its opposite the spot was nearly free from colour\*, while in the other two positions, differing from the former by  $90^\circ$ , the coloration was intense. It was evident that some cause was at work, in one case compensating, and in the other doubling, the usual Brewsterian coloration.

If  $M_0$  be the mean value of  $M$ , the setting of the nicols will give, as before,

$$\tan \alpha \tan \beta = \mp M_0/S; \quad (16)$$

while from (11),

$$T = \pm M_0 \cos \gamma. \quad (17)$$

The angle of reflexion corresponding to darkness is determined by (17), and both sides of the equation are functions of  $\lambda$ . For the mean ray  $\gamma = \pm \frac{1}{2}\pi$ , and at the correct angle  $T=0$ . For a neighbouring ray at the same angle of reflexion we have for  $T$ ,

$$\frac{dT}{d\lambda_0} \delta\lambda;$$

\* Attention is here fixed upon the central plane of incidence, colour on the right and left of the spot being disregarded.



and for  $\cos \gamma$ ,

$$\cos \frac{1}{2} \pi (1 + \delta\gamma/\gamma_0) = -\frac{1}{2} \pi d\gamma/\gamma_0.$$

Hence the condition of achromatism is

$$\frac{dT}{d\lambda_0} \delta\lambda \pm \frac{1}{2} \pi M_0 \delta\gamma/\gamma_0 = 0;$$

or by (15),

$$\frac{dT}{d\lambda_0} \mp \frac{\pi M_0}{2\lambda_0} = 0. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Thus if  $M_0$  be of the right magnitude, the colour will be compensated when  $\gamma = \frac{1}{2} \pi$ , and doubled when  $\gamma = -\frac{1}{2} \pi$ , or *vice versa*.

When the colours were but little dispersed in the plane of incidence, there could usually be observed on sufficiently contaminated surfaces a dispersion laterally, indicating a variation of  $M$  with  $\lambda$ . It was to be expected that  $M$  should be proportional to  $\lambda^{-1}$ . Not much more could be done experimentally than to verify the direction and order of magnitude of the effect. Thus it appeared that on a greasy surface the difference of readings corresponding to  $\beta = +30^\circ$  was greater when the settings were made for the brown than for the blue side of the spot. Of these the former, due to the *absence* of blue, represents the setting proper to blue light.

The angles  $+30^\circ$  were found suitable for  $\beta$ . It was at first supposed that advantage would accompany a smaller  $\beta$ ; but in this case the spot was too diffused in a horizontal direction to suit the dimensions of the bright field employed. The adjustment of the spot to centrality (right and left) by variation of  $\alpha$  was then less certain. On the other hand, a too great increase of  $\beta$  throws excessive stress upon the readings of  $\alpha$ .

The delicacy of the apparatus may be measured by the smallest error of  $\alpha$  visible on simple inspection. When the light was bright and the reflecting surface steady, a setting for  $\beta = +30^\circ$  was visibly wrong on going over to  $\beta = -30^\circ$ , when the change afterwards found necessary in the setting of  $\alpha$  exceeded about  $2'$ . Less than this could hardly be recognized on simple inspection; but the error of a single setting, arrived at by trials backwards and forwards, appeared to be less than  $1'$ . Thus the same readings, taken to the nearest minute, were often recovered many times in succession; but on other occasions larger differences were met with, and it was often difficult to judge whether they were due to imperfect observation or to real changes in the condition of the reflecting surface. In any case it will be a modest estimate

## 14 Lord Rayleigh on *Reflexion from Liquid Surfaces*

to suppose that a difference of one minute in  $\alpha$  can be detected on repetition. From this we should get, by (14), as the least observable value of  $k$ ,

$$k = \frac{1}{2} \tan 30^\circ \times \tan 1' = .00009.$$

Jamin's arrangements do not appear to have allowed of the determination of values of  $k$  less than .001.

The first systematic experiments upon cleaned water-surfaces showed that the ellipticity, if real, was pretty close to the limit of observation. At this stage I expected to find the marked ellipticity of greasy water gradually diminishing to zero as the purifying process was carried further, but remaining always of the same sign, so long as it could be observed at all. This anticipation was not completely verified. The larger differences of  $\alpha$ , found with ordinary water upon which camphor fragments were fully active, amounting say to  $40'$ , rapidly diminished under the skimming process, so that the final difference on the purest surfaces seemed just to escape direct observation. It frequently happened that no displacement of the dark spot relatively to the cross wires could be detected on the reversal of  $\beta$ . But when, in order to the highest accuracy, many sets of alternate readings were taken, the difference would come out sometimes in one direction and sometimes in the other. A small difference of  $2'$ , or more, on the side of the contaminated water was easily accepted as due to incomplete cleaning, but I was for a time sceptical as to the significance of similar small differences in the opposite direction. That these differences were not errors of observation was soon apparent; but I thought that they might be of instrumental origin, due perhaps to some mal-adjustment.

The outstanding question was so small that it might perhaps have been dismissed, but I was unwilling to stop without a determined attempt to get to the bottom of it. The minute reversal of ellipticity stood its ground in spite of repeated remountings of the apparatus; but I feared that it might possibly be due to some, though I was unable to conjecture what, defect in the optical parts themselves. When, however, the nicols at first used were replaced by beautiful prisms made by Steeg and Reuter and the effect still remained, it had to be accepted as genuine, and the conclusion was forced upon me that with some water-surfaces, and those presumably the cleanest, there is a minute ellipticity in the opposite direction to that of ordinary water, and such that the difference of settings for  $\alpha$  amounted to about  $2'$ . This corresponds to  $k = +.0002$ . It will be understood that this is a very minute

quantity, but it is not without interest from a theoretical point of view. The fact that  $k$  can be positive as well as negative implies of course its possible evanescence. It is, I think, safe to say that some samples of water-surfaces polarize light to perfection.

It will now be desirable to give a specimen of actual observations. The one selected, principally on account of its completeness in respect to the positions of the quarter-wave mica, is dated April 1, 1891, and relates to a surface of tap-water, freshly drawn, and skimmed with the aid of the brass hoop already described. The operation of skimming was repeated after each readjustment of the mica. In the first column the direction of the arrow indicates the position of the mica. The second gives the readings of  $\beta$ , the third the individual readings of  $\alpha$ , the minutes only being entered\*. It

Mica.	Analyser, $\beta$ .	Polarizer. Separate Readings of $\alpha$ (minutes).	Means.	Difference.
↓	+30 -30	31, 32, 32, 31 28, 29, 29, 29	183 31' 183 28'	+2½
→	+30 -30	28, 31, 29, 30 32, 31, 32, 32	183 29' 183 31'	-2½
↑	+30 -30	33, 33, 33, 33 30, 32, 32, 32	183 33 183 31'	+1½
←	+30 -30	28, 29, 29, 29 31, 32, 31, 29	183 28' 183 30'	-2

will be understood that the readings for  $\beta = \pm 30^\circ$  were taken alternately; the first reading under ↓ being 31', the second 28', the third 32', and so on. The fourth column gives the means, and the fifth the difference of these means, which represents ellipticity. The second and fourth differences, corresponding to positions of the mica differing by a right angle from those of the first and third, must have their signs reversed before combination for a final mean difference. We get

$$\frac{1}{4}(2\frac{3}{4} + 2\frac{1}{4} + 1\frac{1}{2} + 2) = +2\frac{1}{8}'.$$

After the last set the hoop was lifted, so as to allow the return

\* In almost all the observations the settings were made by myself, and the readings of  $\alpha$  at the vernier by Mr. Gordon. Without two observers the difficulties would have been much increased.

of the contamination. The readings then became

$$\leftarrow \begin{array}{c|c|c} +30^\circ & 37, 44, 43 \\ -30^\circ & 17, 14, 12 \end{array} .$$

It would appear that the first of these were premature, insufficient time having been allowed for the contamination to spread. The difference, reckoned as before, may now be taken to be about  $-30'$ , and is in the *opposite* direction to the small effect of the clean surface. For the contaminated surface  $k = -.0026$ , and for the clean  $k = +.00018^*$ .

Although the above results, and others of a similar nature, obtained both with tap-water and with distilled water, render it practically certain that  $k$  is positive for pure water, I do not regard with the same confidence the numerical value above recorded. It is difficult to feel sure that the cleansing was sufficient. A theoretical objection to the hoop method has already been alluded to; and the more perfect methods depending upon the use of convection currents† are scarcely applicable here. Attempts were indeed made to work with a surface cleaned by an ascending column of fluid, the column being expanded by heat communicated to it from an immersed platinum spiral, itself warmed by an electric current. But the readings were not accordant; and it appeared that the observations were prejudiced by the deformations of the surface which are the necessary accompaniment of such a flow. Doubts as to the perfection of the cleanliness actually attained lead me to think it possible that the true value of  $k$  for an ideal water-surface may be even twice as great as that actually found.

Opportunities for useful work upon clean surfaces have been very few, for it is hopeless to attempt observations without a prospect of at least an hour's almost uninterrupted sunshine. But shorter and more uncertain periods may be utilized for observations upon contaminated surfaces, as these do not demand the same care or amount of repetition. As an example of such I will record the readings of June 6, from a water-surface slightly greased with oil of cassia.

\* The observations so far did not of themselves determine which of the two surfaces has the positive  $k$  according to Jamin's convention. It was evident, however, that it must be the contaminated and not the clean surface which corresponds to Jamin's determination of a negative  $k$ . Subsequent observations upon reflexion from glass verified this assumption.

† See Roy. Soc. Proc., "On the Superficial Viscosity of Water," vol. xlviii. p. 133.

↑		+ 30° - 30°		180° 2' 180° 54'		Band achromatic.
←		+ 30° - 30°		180° 47' 179° 59'		Band strongly coloured, red above.

The difference of readings is here about  $-50'$ , giving  $k = -.0043$ . On trial it was found that camphor fragments would just move. The above is an example of the effect of the position of the mica upon the coloration of the band, a subject already discussed.

Experiments were made with the object of comparing different kinds of oil as to their relative effects, optically and upon camphor. It was found, as had been expected, that cassia was more powerful optically than olive-oil. Thus when camphor was nearly dead the difference of readings for olive-oil was about  $-30'$  and for cassia about  $-48'$ .

Interest was felt in the behaviour of a saturated solution of camphor, whose surface-tension is much lower than that of clean water. Observations upon this liquid proved especially difficult, for the dark spot frequently shifted laterally while under inspection, indicating temporary changes in the ellipticity of the particular part of the surface in use. There is little doubt that this complication is due to local evaporation under the influence of light currents of air. As the camphor evaporates from any part of the surface, the tension is momentarily raised, and the surface contracts. If the camphor only were in question, there would probably be no attending optical disturbance, but the local expansions and contractions of the surface lead to attenuation and concentration of the greasy matter present. Under favourable circumstances the difference in the readings of  $\alpha$  might be as low (numerically) as  $-6'$ , and was perhaps due after all to residual greasy matter, other than camphor. In any case the optical effect of the camphor is much less than that of an oily film giving the same surface-tension.

With a strong solution of oleate of soda the difference of  $\alpha$  could not be reduced below  $-25'$ . It is difficult to suppose that this can be due to a film of foreign matter removable by skimming. But the amount of the ellipticity is very low in relation to the surface-tension, which is only about one third of that of clean water. The value of  $k$  corresponding to the above readings is  $-.0021$ , only about double of the smallest quantity appreciated by Jamin.

That the surface-tension has no definite relation to the

*Phil. Mag.* S. 5. Vol. 33. No. 200. Jan. 1892. C

ellipticity is abundantly evident. For example, camphor was quite active upon a surface which gave a difference of readings of  $-80'$ , corresponding to  $k = -.007$ . On this occasion the surface had stood for some time without much protection, and it is possible that the effect may have been partly due to dust.

The last example that I will mention of aqueous solutions is a strong brine. This gave a somewhat variable difference of about  $-5'$ , corresponding to  $k = -.00042$ . In this case there seemed to be unusual difficulty in getting the surface clean, so that the difference between the brine and pure water is not improbably due to some secondary cause.

Most of the available time was spent upon water in its various states, not only on account of its intrinsic importance, but also because of the presumably greater simplicity of a clean water-surface. The observations are made in an atmosphere which contains no very small proportion of aqueous vapour. When the liquid under examination has an affinity for water, *e. g.* alcohol, it is difficult to form a precise idea as to what may be the condition of the surface. Besides, the arrangements for skimming are less easily applied. On the other hand, the liquids of lower tension are less likely to acquire a film of grease. For alcohol, and also for petroleum, the value of  $k$  is about  $+.0010$ .

The general conclusion to be drawn from these investigations is that the ellipticity of the liquids examined is very much less than was supposed by Jamin, whose results for water and aqueous solutions were almost certainly vitiated by the presence of greasy contamination. Thus the intensity of reflexion from clean water is not much more than  $\frac{1}{1000}$  part of that given by Jamin. Moreover, the value of  $k$  is positive, and not negative. It is even possible that there would be no sensible ellipticity for the surface of a chemically pure body in contact only with its own vapour. But the surfaces of bodies are the field of very powerful forces of whose action we know but little; and even if there be nothing that could be called chemical change, the mere want of abruptness in the transition would of itself entail a complication. There is thus no experimental evidence against the rigorous applicability of Fresnel's formulæ to the ideal case of an abrupt transition between two uniform transparent media.

September 19.

POSTSCRIPT (October 11).

Solutions of saponine and gelatine, substances which confer the foaming property, have been examined. With very small quantities the difference of readings may amount to a degree, *not to be diminished by repeated skimming*. The value of  $k$  is thus  $-.005$ .

The suspicion above suggested that the true value of  $k$  for clean water may be numerically higher than is indicated by the results obtained with the aid of the brass hoop has been verified by some observations upon surfaces cleansed by heat. The water, as clean as possible, was contained in a large shallow tin tray. By the application of gentle heat to the part of the tray under optical examination any residual grease is driven off, in consequence of the smaller tension of the warmer surface. If the whole surface is fairly clean to begin with, a very moderate difference of temperature suffices to keep the grease at bay. The difficulties of the experiment have so far prevented a complete series of readings; but the following, obtained on October 2, seem sufficient to establish the fact:—

→		+ 30°		43, 42, 42, 42
		− 30°		47, 47, 48, 47
↑		+ 30°		52, 51, 51, 50
		− 30°		47, 46, 47, 45, 48

At the conclusion of the second set the contamination was evidently returning. It would seem that on the cleanest surfaces the difference of readings may amount to 5', the necessity of readjustment on passing between  $\beta = \pm 30^\circ$  being obvious on simple inspection. Corresponding to this

$$k = +.00042.$$

Terling Place, Witham.

II. *On the Character of the Light emitted by Incandescent Zinc Oxide.* By EDWARD L. NICHOLS and BENJAMIN W. SNOW\*.

IN a recent paper on the influence of temperature on the colour of pigments†, we described the singular changes which rise of temperature produces in the character of the light

\* Communicated by the Authors.

† Phil. Mag. [5] vol. xxxii. p. 401.

reflected by the oxide of zinc (p. 420). The results obtained in that investigation led us to the conclusion that certain fluctuations in reflecting-power were indications of peculiarities in the law of the effect of heat on the radiating-power of the oxide. In the present paper we purpose to describe an attempt to verify that conclusion by the application of the same method of observation to the study of the visible radiation at temperatures between  $650^{\circ}$  and  $1000^{\circ}$  C.

Almost the only material, the radiation of which as a function of the temperature has been determined quantitatively, is platinum. In 1879 one of the present writers described some photometric measurements of the light emitted by that metal\*. In the same year Violle† published data concerning the total radiating-power, between  $800^{\circ}$  and  $1775^{\circ}$  C., without entering upon the question of the changes in the quality of the light. In the same year also Jacques‡ attacked the problem of the distribution of energy in the spectrum of various incandescent solids, extending the investigation to platinum and certain oxides of copper, iron, chromium, and aluminium. Dr. Jacques used the thermo-pile and galvanometer in his measurements, and dealt more particularly with the energy-curves of the infra-red. In 1881 Violle§ published readings for four regions of the visible spectrum ( $\cdot 656$ ,  $\cdot 589$ ,  $\cdot 535$ ,  $\cdot 482$ ), the source of light being platinum at  $775^{\circ}$ ,  $954^{\circ}$ ,  $1045^{\circ}$ ,  $1500^{\circ}$ , and  $1775^{\circ}$ . The source of comparison was the carcel lamp.

None of the existing data gave the law for platinum with sufficient definiteness for our purpose, which was to compare the radiation of the zinc oxide, wave-length by wave-length, with that emanating from platinum at the same temperature, throughout the entire range of temperatures already indicated. Measurements of the platinum spectrum were accordingly made at several stages of incandescence. From these measurements a set of curves were plotted, which gave graphically the increase of radiating-power with rise of temperature for each of nine selected regions of the spectrum. The ordinates of these curves are relative light-intensities, the abscissæ are degrees of the centigrade thermometer. For convenience, the intensity of the region of the D line of Fraunhofer, when the metal is at the temperature of  $1000^{\circ}$ , has been selected as unity. The comparison lamp was an incandescent lamp held

\* E. L. Nichols, *Ueber das von glühendem Platin ausgestrahlte Licht*. Dissertation: Göttingen, 1879.

† J. Violle, *Comptes Rendus*, lxxxviii. pp. 171-173.

‡ W. W. Jacques, "Distribution of Heat in the Spectra of various Sources of Radiation." *Proc. Amer. Acad. of Arts and Sc.*, 1879.

§ J. Violle, *Comptes Rendus*, xcii. pp. 886 and 1206.



at a constant voltage, the temperature being below normal to secure permanence. The quality of the light was not very different from that of an ordinary luminous gas-flame.

Similar measurements to the above upon the spectrum of the light radiated from a surface of zinc oxide, the wavelengths selected being the same as those in the platinum spectrum, made it possible to compare the radiating-power of the two materials, when subjected to the same conditions of temperature.

The apparatus and the method used have been described in detail in the paper on the Colour of Pigments, just cited. In our determination of colour at high temperatures, a film of the oxide which had been prepared by smoking a strip of platinum foil over the flame of burning zinc was heated to the desired degree by the action of an electric current upon the foil. The surface of the oxide was illuminated by means of an incandescent lamp, and the spectrum of the reflected light was compared with that of another lamp similar to the first. In the experiments to be described in this paper, the first lamp was dispensed with, and a study was made of the light from the glowing surface itself. Since the rays to be measured were for the most part very feeble, it was necessary to carry on the experiments in a perfectly dark room. Temperatures, as in our study of colour, were determined from the expansion of the foil.

The measurement of the temperature of incandescent foil by means of the expansion of the metal is somewhat less sensitive than the method of change of electric resistance, but it is much to be preferred to the latter whenever a direct calibration of the metal by reference to the air-thermometer, or to the melting-point of metals, is impracticable; for the reason that the coefficient of expansion is much less affected by traces of impurity than the resistance coefficient is. A comparison of the various formulæ proposed for the calculation of the temperature of platinum from its electrical conductivity, is in itself sufficient to show the importance of the direct calibration. Two specimens of platinum, which had been ordered for the purpose from two well-known dealers, who had been informed of the use to which the wire was to be put and requested to pay especial attention to the matter of the purity of the samples, were thus tested in the physical laboratory of Cornell University by Mr. Ernest Merritt. The curves for resistance and temperatures obtained were widely different, the one being convex and the other concave to the base-line of temperatures. Any single formula for temperature, applied to these two wires, would have given

values which at one thousand degrees were more than one hundred degrees apart. We think that the well-known formula of Matthiesen,

$$l = l_0(1 + \cdot 00000851 t + \cdot 0000000035 t^2),$$

which we made use of in these experiments, may be applied to any commercial specimen of platinum, of reasonable purity, without the introduction of such serious errors, and that, whatever may be the general correction which it may be found necessary to apply to that formula, in order to obtain temperatures in absolute measure, it will always be possible for any one knowing the formula used to be sure of the approximate temperatures, without reference to the character of the individual piece of platinum employed.

Table I. contains the relative intensities of the platinum spectrum between 700° and 1000° C. The reference standard was the incandescent lamp already referred to, and the intensity of the region of the D line of the platinum spectrum was taken as unity throughout. Table II. gives the intensities of the spectrum of the film of zinc oxide for the same wavelengths and the same range of temperatures. The results are presented graphically in figs. 1 to 6, six of the nine wavelengths being plotted. In these figures the isochromatic curves of platinum and of the oxide are plotted side by side to facilitate comparison. The curves for platinum are smooth and all of the same type. They agree in all essentials with those obtained from the measurements described in the articles already cited (Nichols, 1879, and Violle, 1881). The corresponding curves for zinc oxide, however, are all broken at a point in the neighbourhood of 880°, at which temperature the radiating-power evidently undergoes sudden and marked increase, continuing with further rise of temperature to follow a law different from that which prevailed at lower temperatures. It will be noticed, moreover, that in the extreme red ( $\lambda = \cdot 713$ ) the platinum is brighter throughout the entire range of temperature than the oxide. The succeeding curves, however, cut each other at 1000° ( $\lambda = \cdot 638$ ), at 920° ( $\lambda = \cdot 587$ ), at 755° ( $\lambda = \cdot 511$ ), and at some lower temperature than 700° for the blue and violet. Throughout the entire range the colour of the oxide is whiter, that is to say, it is relatively richer in the shorter wave-lengths than the light from platinum at the same temperature. There is in the case of the oxide a region of comparative feebleness in the yellow and green, corresponding to the region of maximum reflecting-power in the heated solid. To every one who has watched the striking behaviour of zinc oxide under the blowpipe-flame, the effects

of which these curves give us definite graphical expression are familiar phenomena. The fading away of the beautiful white glow of the film into the greenish-yellow of the cooler oxide, without the intermediate redness which most bodies display as they pass from higher temperatures through the range of temperature which goes by the name of the red heat,

Fig. 1.

Fig. 2.

Fig. 3.

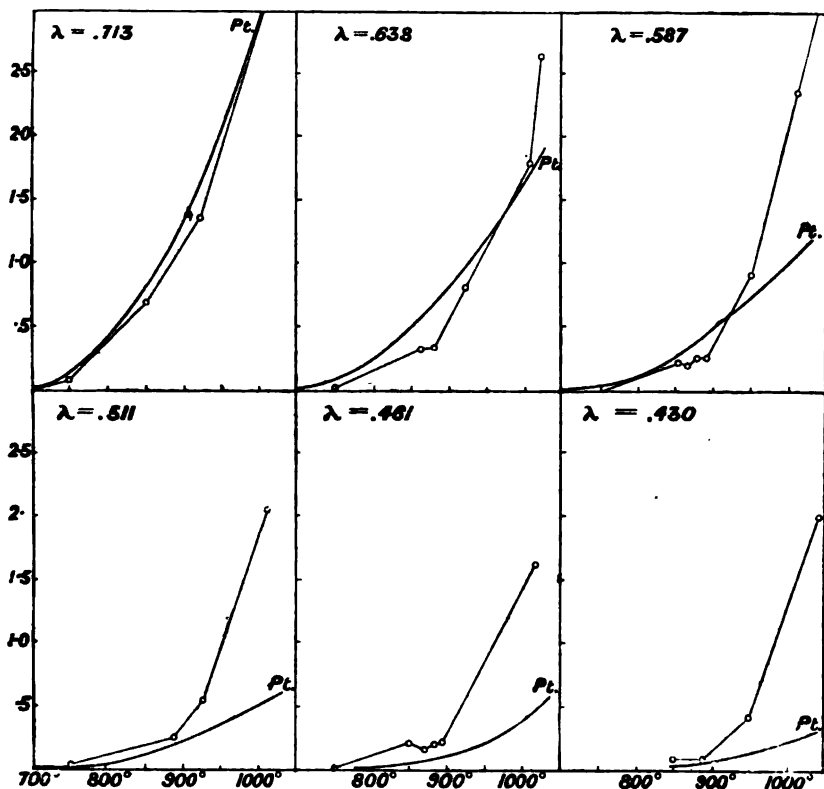


Fig. 4.

Fig. 5.

Fig. 6.

**Isochromatic Curves for Zinc Oxide and Platinum (700° to 1000°).**

is caused by the gradual overpowering of the rapidly diminishing radiated light by that due to reflexion. A remarkable feature brought out by these isochromatic curves is the performance of the film between 800° and 880°. Within that range the change of radiating-power increases but slowly as

the temperature rises. Suddenly, then, follows the outburst of radiant energy which begins at the latter temperature.

TABLE I.—Intensity of the Radiation from Platinum at various Temperatures, in terms of the radiation of like wave-lengths from an incandescent lamp. The intensity of the region  $\lambda=587$  in the spectrum of platinum at  $1000^\circ$  is taken as unity.

Wave-lengths.	1000°.	950°.	900°.	850°.	800°.	750°.	700°.	650°.
713	2.78	2.02	1.33	.802	.409	.121	.033	
638	1.56	1.11	.795	.489	.229	.073	.008	.003
587	1.00	.725	.482	.253	.101	.035	.005	
544	.659	.479	.316	.174	.059	.010	.002	
511	.444	.330	.222	.121	.042			
484	.333	.232	.139	.069	.021			
461	.278	.180	.101	.042	.010			
444	.229	.149	.080	.028				
430	.201	.135	.069	.021				

TABLE II.—Intensity of the Radiation from the Oxide of Zinc at various Temperatures, in terms of the radiation of like wave-lengths from an incandescent lamp. The intensity of the region  $\lambda=587$  in the spectrum of glowing platinum at  $1000^\circ$  is taken as unity.

Wave-lengths.	1038°.	1013°.	925°.	884°.	868°.	848°.	739°.	707°.
713	.....	3.026	1.332	.....	.....	.708	.084	.034
638	2.605	1.985	.891	.343	.313	.....	.088	.013
587	2.778	2.443	.659	.281	.235	.250	.019	.007
544	2.504	.....	.391	.278	.178	.....	.011	.003
511	1.880	2.064	.565	.288	.190	.221	.010	.0015
484	2.013	.....	.453	.283	.178	.185	.005	.0008
461	.....	1.620	.....	.214	.160	.188	.003	
444	2.054	.....	.420	.179	.108	.111		
430	2.002	.....	.420	.097	.093	.091		

The character of the colour of the incandescent zinc oxide can be given more explicit expression by means of isothermal curves, in which the distribution of intensities throughout the visible spectrum is shown for a given temperature, than in those which have just been presented. Three ways of drawing these curves offer themselves. The absolute distribution of intensities may be given, the resulting curves being such as would be obtained by exploring the spectrum with a

sufficiently sensitive thermopile; or the intensities may be expressed in terms of those of the comparison-lamp, wave-length for wave-length; or, finally, one may express the curve for each temperature in terms of the radiation from platinum at the same temperature, wave-length for wave-length. Our knowledge of the spectrum of the incandescent lamp was not accurate enough to enable us to adopt the first of these methods, which is moreover not so well adapted for the graphic expression of colour as is the second one. The third method offers the advantage of a direct comparison between the light from platinum and from the oxide under like conditions of incandescence.

In figs. 7, 8, and 9 the second method has been adopted.

**Isothermal Curves for the Radiation from Zinc Oxide and Platinum;** showing three stages in the development of the radiating-power of the former substance. Ordinates are intensities in terms of those of corresponding wave-lengths in the spectrum of the comparison-lamp.

Fig. 7.

Fig. 8.

Fig. 9.

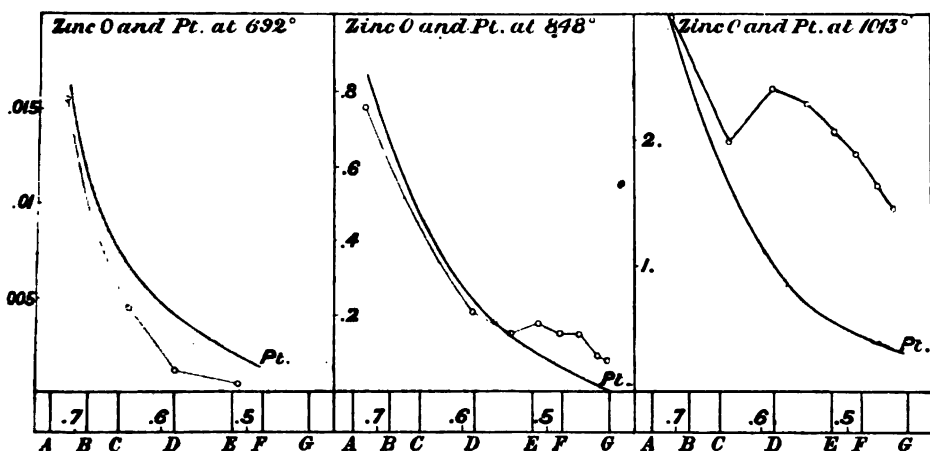


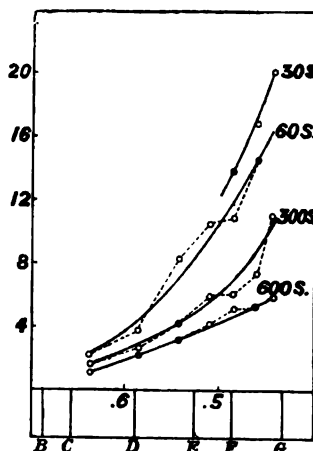
Fig. 7 gives typical curves for a temperature below  $700^{\circ}$ , at which stage the radiation from the oxide is weaker throughout the spectrum than that from platinum. Fig. 8 contains the corresponding curves for  $848^{\circ}$ , at which temperature the green, blue, and violet are stronger in the spectrum of the oxide than in that of the platinum. In fig. 9 the spectrum of the film of the oxide, which has been maintained at  $1013^{\circ}$  for ten minutes, is compared with the platinum spectrum for the same temperature. The measurements of the oxide are

simultaneous. At this stage the luminescence of the oxide is very marked. In these diagrams ordinates express the brightness of each wave-length in terms of that of the corresponding wave-length in the spectrum of the comparison-lamp.

In the course of our experiments it was found to be more and more difficult to obtain consistent measurements as the temperature of the film increased; and it soon became evident that we had to deal with an unstable state of incandescence, the oxide being much brighter when first ignited than at any later period. The changes were most rapid during the first ten minutes after the foil was brought to incandescence, after which time the rate of change was not such as seriously to interfere with the accuracy of the determinations. All the results given thus far were obtained from films which had been heated for a sufficient time to ensure their permanence. Values for films freshly ignited were also obtained. They were always higher than those of the older films. Such results, owing to the fact that they pertained to surfaces the radiation of which was fugitive, have been excluded from the tables and curves. It was deemed desirable, however, to determine as accurately as possible the manner in which the incandescence of fresh films diminished as a function of the time. For this purpose a set of rapid readings were made. A film newly prepared was ignited, and settings of the intensity were made at intervals of ten seconds from the time when the current was applied. These readings were less accurate than those made at leisure, and one setting, instead of a series of five or ten, had to be taken to represent the radiation at a given instant of time. The same method was then pursued for another wave-length, a fresh film being prepared for the purpose, and this was repeated until a series of time-curves were secured which included the entire spectrum. The results for each wave-length gave a curve showing the rate of diminution with the time. The curves were all of the same general type; but they showed the time-effect to be least in the red, and to increase as the wave-length of the region observed decreased. From these data it was also possible to construct a series of intensity-curves, showing the relative brightness of the spectrum and its character at any given time between the limits covered by the observations. These curves for thirty seconds, sixty seconds, three hundred seconds, and six hundred seconds from the moment of ignition of the oxide are given in fig. 10. They bring out in the most striking way the evanescent character of the light emitted by the oxide at the temperature in question, which was  $1013^{\circ}$ . This "time-effect" became very noticeable at about  $900^{\circ}$ ; and it seems

most probable that it indicates a peculiarity of the radiation which begins to show itself at that temperature and which causes the sudden rise in the curves of figs. 1 to 6. In fig. 10 the third method of plotting was used. Platinum at

Fig. 10.—Radiations from Zinc Oxide at 1013°, as a function of the time. Ordinates give the intensity of each wave-length in terms of that of the radiation from platinum (wave-length for wave-length) at the same temperature.



1013°, instead of the comparison-lamp, was the reference-standard, and the ordinates of the curves give the ratio of the intensity of each region of the spectrum of the zinc oxide to that of the corresponding wave-length in the spectrum of the glowing metal.

We think it evident from these experiments that in zinc oxide one has to do with a material which, in addition to the ordinary incandescence due to temperature, is highly luminescent above 880°. The phenomenon is of the class which Becquerel and other of the earlier students of the subject have described as "phosphorescence by heat." Owing to the presence of the ordinary incandescence at such temperatures, this property of zinc oxide seems hitherto to have escaped investigation; although it has of course been noticed by every one acquainted with blowpipe reactions that the oxide, when heated, emits a light which is very different from that of carbon, or of most substances with the incandescence of which we are familiar.

There are good reasons for supposing that other of the metallic oxides will show peculiarities of radiation when

heated, similar to those exhibited by the oxide of zinc. Cylinders of lime, for example, when freshly ignited in the oxyhydrogen flame, attain a momentary brilliancy and whiteness which is not reached during any subsequent ignition.

The extraordinary brightness of the magnesium flame also is undoubtedly to be ascribed to a state of initial incandescence such as that which we have observed in zinc oxide. W. H. Pickering\* found the character of the light of burning magnesium to be that corresponding to a temperature considerably above  $3000^{\circ}\text{C}$ . Recent measurements of the actual temperature of the flame, however, show that it is not above  $1400^{\circ}\text{C}$ .

Other instances of abnormal incandescence of the metallic oxides might be cited. At what temperatures the effect occurs, and what its precise nature is in the case of the various substances in which the phenomenon presents itself, must be determined by further experiment.

Physical Laboratory of Cornell University,  
June 1891.

### III. *A Method of Measuring Loss of Energy due to Chemical Union &c.* By Dr. G. GORE, F.R.S.†

IN this research a number of pairs of electrolytic substances, in some cases acids and alkalies, were selected, and the conditions of the experiments so arranged that the relative mean amount of loss or gain of energy of each pair of substances during their act of chemical union, mixture, or mutual decomposition whilst in solution, might be measured by means of a small voltaic couple and the null method of balance, with the aid of a suitable thermoelectric pile (see Proc. Birm. Phil. Soc. vol. iv. p. 130, 'The Electrician,' 1884, vol. xii. p. 414) and an astatic galvanometer having 100 ohms resistance in its coils. The voltaic couple consisted of a suitable positive metal and platinum, and was lowered into and raised out of the electrolyte by means of a rack and pinion. The positive metals usually employed were aluminium, tin, cadmium, zinc, and magnesium. A little improvement in the thermopile was used in this research; it consisted in passing a stream of cold water through a pipe immersed in the cold oil-bath and thus keeping it at a constant temperature.

The following is an outline of the method:—1st. Take a con-

\* Proc. Amer. Acad. Arts and Sci. 1880.

† Communicated by the Author.



venient quantity of an acid, such as an equivalent weight in grains, dissolve it in about two thousand grains by weight of distilled water, measure the electromotive force of a small voltaic couple of aluminium and platinum in the liquid and call the amount "A." 2nd. Take a chemically equivalent weight of an alkali, dissolve it in an equal quantity of water, measure the electromotive force of the couple in the solution and call the amount "B." 3rd. Take an equivalent weight of the salt resulting from the union of the acid and alkali dissolved in the same quantity of water, measure the electromotive force in a similar manner and call the amount "C." We have now the electromotive force "A" excited by the acid; "B" by the alkali; and "C" by the salt formed by their union. 4th. Multiply the electromotive force "A" by the equivalent weight of the acid, and the one "B" by that of the alkali, add the two products together, and divide the sum by that of the two equivalent weights, and call the quotient "D." "C" represents the mean electromotive force excited by the compound as found by means of experiment, and "D" that arrived at by calculation. 5th. Subtract the experimental amount "C" from the calculated one "D" (or the reverse, as the case may be), and a difference remains which represents the relative amount of loss (or gain) of energy which has occurred during the act of chemical union, change, or mixture of the acid and alkali or other substances employed, as measured by the particular positive metal. And, 6th. Ascertain the percentage amount of loss or gain of the calculated electromotive force "D" in various cases. By this process we obtain a series of percentage numbers which we may view as representing the relative amounts of loss (or gain) of molecular energy which have occurred during the actions with the different substances under the given conditions.

The method is essentially one for directly measuring the differences of mean amount of electromotive force excited by two different electrolytes, and by the liquid produced by mixing them together, with particular positive metals, before and after mixing; and as these differences must indicate the quantity of energy of some kind lost or gained during the mixing, the method is to a corresponding extent a means of ascertaining the amount of relative loss or gain of energy during the chemical union or mixture of electrolytes. If we use only a single kind of positive metal, the method may be regarded as a system of measurement of the relative losses and gains of energy as obtained by means of that particular metal. Each positive metal is probably only affected by

and only measures the influence and changes of a portion of the molecular motion of the substances present, viz. that portion which neutralizes some of the molecular motion of that metal and converts it into electric current. In a research on "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c. of Electrolytes" (Phil. Mag., August 1891, p. 157), I have shown that in various cases of dilution or mixture of such liquids, a *gain* of mean amount of electromotive force of the two liquids occurs simultaneously with a *loss* of latent heat during the act of mixing, the kind of energy therefore measured by this method is not identical with that of heat; and as we do not know definitely of what "chemical affinity" really consists, we cannot say that what is measured is identical with chemical energy. Whilst the thermochemical method only measures the proportion of energy which causes thermal change, the present one only measures that which produces electric change; and it is probable that the kind of energy measured differs somewhat with each different kind of positive metal. That we are unable clearly to define either of the fundamental kinds of energy, and that the modifications of them are very numerous, is generally admitted.

A number of suitable pairs of acids and bases, acids and carbonates, acids and salts, &c. were examined with different positive metals according to this method, and the percentage amounts of loss or gain of molecular energy ascertained. All the measurements of electromotive force are given in volts. The means employed of obviating undue influence of polarization have already been described (Phil. Mag., Dec. 1890, p. 484), and were sufficiently effectual in nearly all cases.

It would have saved much labour, and have yielded more simple and apparently more important results, if the measurements had been limited to those obtained with a single positive metal. But whilst taking great care to obtain substantially reliable results, I have avoided making only a small number or a very limited variety of experiments, because it imparts a false degree of apparent consistency and importance to the results, and leads to the common and erroneous conclusion that the phenomena of nature are more simple than they really are, and consequently the conclusions drawn have to be sooner or later corrected. In an extensive subject like the present one, a considerable number and sufficient variety of facts is necessary in order to arrive at truthful conclusions.

The substances employed were in nearly every case of a high degree of purity. Distilled water was used in making all the solutions. The *cæsium* carbonate was obtained from Dr. H. Trommsdorff, of Erfurt, and both it and the carbonate

of rubidium were converted into caustic by means of sulphuric acid followed by baryta. The solution of caustic soda was prepared by adding small fragments of sodium to water in a covered nickel crucible. Chlorate of rubidium could not be used, because it was not sufficiently soluble; carbonic acid, chlorine, and iodine were too insoluble to form solutions of the usual degree of strength, and weaker solutions had to be employed.

The results are given in series of tables. The quantities of substances used in each single table were chemically equivalent to one another, and those of one table were usually so to those of other tables, except in certain cases which the reader will have to observe. "Strong solutions" contained 1 equivalent weight in grains dissolved in 1800 grains of water; in consequence of the sparing solubility of carbonic acid, the "weak solutions" were arranged to contain only one tenth that quantity or 1 equivalent weight in 18,000 grains of water. In Tables XVI., XVIII., XIX., XX., XXII., XXIII., XXIV., XXV., XXVIII., and XXIX. still weaker liquids were used. In all the tables, as the amounts of variation of electromotive force due to difference of atmospheric temperature were usually small (see page 42), and the insertion of the temperatures would enlarge the tables, the temperatures are omitted.

In most of the tables of Sections A, B, C, and D, the substances are arranged in the usual chemical groups in order to enable the results to be more conveniently compared with the atomic weights, specific gravities, amounts of chemical heat, &c. of the elementary constituents of the compounds.

The tables of Section A relate to the Formation of Salts from Acids and Alkalies, and give with each pair of substances the separate amounts of electromotive force excited by the acid, the base, and the saline product of their union; then the mean electromotive force as calculated from those of the two separate substances and corrected for difference of equivalent weight; the amounts of loss of energy due to the chemical union of the acid and base, and the percentages of such loss upon the calculated mean amounts. In some of these tables, the numbers of Centigrade-gramme units of heat evolved by the chemical union of some of the same ingredients, as determined by J. Thomsen, are given for the purpose of comparison with the amounts of loss of electromotive force.

The influence of the positive metal was examined by employing several different positive metals with the same solutions in different sections of the research. The effects of difference of acid, base, salt, halogen, strength of solution,

temperature, and heating the liquids were also examined. Aluminium is a suitable positive metal to use with the alkalis.

### Section A.—FORMATION OF SALTS FROM ACIDS AND ALKALIES.

TABLE I.—*Positive metal, Aluminium.* Strong Solutions.

Ingredients.	E.M.F.	Compounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.	Units of Chemical Heat.
CsHO.	1.44148						
RbHO.	1.41000						
KHO.	1.38140						
NaHO.	1.39140						
AmHO.	1.36138						
HCl.	1.12986	CsCl.	.9238	1.9838	Loss .460 = 33.33		
		RbCl.	1.0090	1.3361	" .3271 24.48		
		KCl.	1.0096	1.2821	" .2725 21.25		202,320
		NaCl.	.9953	1.2666	" .2713 21.40		193,020
		AmCl.	.9381	1.2585	" .3204 25.45		
HBr.	1.0954	RbBr.	.9810	1.2707	Loss .2897 = 22.80		
		KBr.	1.0382	1.2123	" .1741 14.35		180,460
		NaBr.	.95526	1.1106	" .15534 13.98		171,160
		AmBr.	.8952	1.1818	" .2866 24.25		
HI.	.9667	RbI.	.8809	1.1623	Loss .2814 = 24.21		
		KI.	.9095	1.0983	" .1888 17.19		150,040
		NaI.	.89506	1.0678	" .17274 16.18		140,600
		AmI.	.86374	1.1160	" .25226 22.60		
H <sub>2</sub> SO <sub>4</sub> .	1.08396	Cs <sub>2</sub> SO <sub>4</sub> .	.92094	1.3570	Loss .436 = 32.13		
		Rb <sub>2</sub> SO <sub>4</sub> .	.92952	1.3022	" .37268 28.62		
		K <sub>2</sub> SO <sub>4</sub> .	.92080	1.2426	" .3218 25.96		267,180
		Na <sub>2</sub> SO <sub>4</sub> .	.91808	1.2221	" .30402 24.87		257,070
		Am <sub>2</sub> SO <sub>4</sub> .	.9095	1.1976	" .2881 24.05		
HNO <sub>3</sub> .	1.0382	CsNO <sub>3</sub> .	.91236	1.3267	Loss .41434 = 31.23		
		RbNO <sub>3</sub> .	.91236	1.2690	" .35564 28.04		
		KNO <sub>3</sub> .	.9095	1.20812	" .29862 24.71		225,930
		NaNO <sub>3</sub> .	.9095	1.1850	" .2755 21.24		216,450
		AmNO <sub>3</sub> .	.9066	1.16178	" .25518 21.98		
HClO <sub>3</sub> .	1.0382	KClO <sub>3</sub> .	.88948	1.1750	Loss .2855 = 24.30		
		NaClO <sub>3</sub> .	.89948	1.1516	" .26212 22.76		
		AmClO <sub>3</sub> .	.8952	1.1309	" .2357 20.84		
Formic acid.	.7379	Cs Formiate.	.73504	1.2832	Loss .54816 = 42.72		
		Rb "	.74934	1.2011	" .45176 37.61		
		K "	.7552	1.0911	" .3359 30.78		
		Na "	.75506	1.0416	" .28654 27.52		
		Am "	.75506	1.0028	" .24774 24.70		

TABLE II.—*Positive metal, Aluminium. Weak Solutions.*  
*Influence of Dilution.*

Ingredients.	E.M.F.	Compounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HCl.	1·0096	KCl.	·9180	1·2035	Loss ·28542 =	23·71
HBr.	·9667	KBr.	·89234	1·1179	„ ·22565	20·17
HI.	·86946	KI.	·85516	1·0122	„ ·15704	15·51
H <sub>2</sub> SO <sub>4</sub> .	1·0382	K <sub>2</sub> SO <sub>4</sub> .	·87232	1·1938	Loss ·3215 =	26·93
HNO <sub>3</sub> .	·9310	KNO <sub>3</sub> .	·85802	1·1452	Loss ·2872 =	25·07
Formic acid.	·7818	K Formiate.	·78080	1·0827	Loss ·3019 =	27·88
The degree of strength of the solutions manifestly affected the results.						
H <sub>2</sub> CO <sub>3</sub> .	·80368					
RbHO.	1·3242	Rb <sub>2</sub> CO <sub>3</sub> .	·92094	1·1673	Loss ·2463 =	21·15
KHO.	1·3299	K <sub>2</sub> CO <sub>3</sub> .	·89520	1·0983	„ ·2031	18·31
NaHO.	1·3385	Na <sub>2</sub> CO <sub>3</sub> .	·89806	1·0583	„ ·16024	15·14

TABLE III.—*Positive metal, Tin. Strong Solutions.*

Ingredients.	E.M.F.	Compounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.	Units of Chemical Heat.
RbHO.	·9210						
KHO.	·9210						
NaHO.	·90384						
AmHO.	·88668						
HCl.	·8066	RbCl.	·75512	·8908	Loss ·1357 =	15·23	
		KCl.	·7494	·8758	„ ·1264	14·43	202,320
		NaCl.	·7351	·8574	„ ·1223	14·26	193,020
		AmCl.	·7065	·8452	„ ·1387	16·42	
HBr.	·79802	RbBr.	·7351	·8665	Loss ·1814 =	15·16	
		KBr.	·7494	·8629	„ ·1135	13·15	180,460
		NaBr.	·73796	·8330	„ ·09504	11·40	171,160
		AmBr.	·68362	·82423	„ ·1406	17·05	
HI.	·73510	RbI.	·6779	·8175	Loss ·1396 =	17·07	
		KI.	·68934	·7917	„ ·10236	12·98	150,040
		NaI.	·6922	·7752	„ ·0830	10·58	140,600
		AmI.	·67504	·7669	„ ·09186	12·97	
H <sub>2</sub> SO <sub>4</sub> .	·8209	Rb <sub>2</sub> SO <sub>4</sub> .	·71794	·8885	Loss ·1706 =	19·20	
		K <sub>2</sub> SO <sub>4</sub> .	·71794	·8742	„ ·15626	17·87	267,180
		Na <sub>2</sub> SO <sub>4</sub> .	·70364	·8581	„ ·15446	18·00	257,970
		Am <sub>2</sub> SO <sub>4</sub> .	·69506	·8478	„ ·15274	18·01	

Table III. (continued).

Ingredients.	E.M.F.	Compounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.	Units of Chemical Heat.
HNO <sub>3</sub> .	·8352	RbNO <sub>3</sub> .	·68648	·9367	Loss ·2502	= 26·71	225,930 216,450
		KNO <sub>3</sub> .	·68362	·8755	" ·1919	21·91	
		NaNO <sub>3</sub> .	·68016	·8618	" ·18164	21·07	
		AmNO <sub>3</sub> .	·68016	·8532	" ·1730	20·28	
HClO <sub>3</sub> .	·8123	KClO <sub>3</sub> .	·6636	·8863	Loss ·2227	= 25·13	
		NaClO <sub>3</sub> .	·6636	·8417	" ·1781	21·16	
		AmClO <sub>3</sub> .	·66932	·8336	" ·1643	19·70	
Formic acid.	·5492	Rb Formiate.	·4862	·8054	Loss ·3192	= 39·63	
		K "	·4920	·7533	" ·2613	34·69	
		Na "	·4920	·7677	" ·2757	35·90	
		Am "	·51774	·6926	" ·1749	25·10	

TABLE IV.—Positive metal, Cadmium. Strong Solutions.

Ingredients.	E.M.F.	Com- pounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HClO <sub>3</sub> .	1·0645	KClO <sub>3</sub> . NaClO <sub>3</sub> . AmClO <sub>3</sub> .	·89004 ·88146 ·88432	·9962 1·0128 1·0080	Loss ·10616	= 10·65
KHO.	·88432				" ·1313	12·97
NaHO.	·87860				" ·12368	12·27
AmHO.	·87288					
Formic acid.	1·0645	Rb Formiate.	·6784	·8448	Loss ·1664	= 19·20
RbHO.	·88432	K "	·6784	·8172	" ·1388	16·98
		Na "	·68126	·8021	" ·12084	15·06
		Am "	·7070	·7939	" ·0869	10·94
Acetic acid.	1·0645	K Acetate.	·9644	1·008	Loss ·0436	= 4·32

TABLE V.—Positive metal, Zinc. Strong Solutions.

Ingredients.	E.M.F.	Com- pounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HClO <sub>3</sub> .	1·3558	KClO <sub>3</sub> . NaClO <sub>3</sub> . AmClO <sub>3</sub> .	1·1699 1·19278 1·18992	1·3200 1·2560 1·2688	Loss ·1501	= 11·37
KHO.	1·2185				" ·0632	5·03
NaHO.	1·21556				" ·0789	6·22
AmHO.	1·1985					
Formic acid.	1·0698	Rb Formiate.	1·04406	1·0520	Loss ·0079	= ·75
RbHO.	1·24426	K "	1·04978	1·1514	" ·10162	8·82
		Na "	1·04692	1·0591	" ·01218	1·15
		Am "	1·05264	1·0624	" ·00976	·91
Acetic acid.	1·3844	K Acetate.	1·20136	1·3905	Loss ·1892	= 13·60

TABLE VI.—*Positive metal, Zinc.* Weak Solutions.

Ingredients.	E.M.F.	Com- pounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
H <sub>2</sub> CO <sub>3</sub> .	1.13844					
RbHO.	1.01830	Rb <sub>2</sub> CO <sub>3</sub> .	1.00974	1.0545	Loss .04476 =	4.21
KHO.	1.01546	K <sub>2</sub> CO <sub>3</sub> .	.9840	1.06957	" .08557	8.0
NaHO.	1.00688	Na <sub>2</sub> CO <sub>3</sub> .	.9697	1.0757	" .1060	9.85

TABLE VII.—*Positive metal, Magnesium.* Strong Solutions.

Ingredients.	E.M.F.	Com- pounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
KHO.	1.4929					
Formic acid.	1.6416	K Formiate.	1.5558	1.5600	Loss .0042 =	.28
Acetic "	1.9592	K Acetate.	1.7131	1.7427	" .0296	1.12

TABLE VIII.—*Positive metal, Magnesium.* Weak Solutions.

Ingredients.	E.M.F.	Com- pounds.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
H <sub>2</sub> CO <sub>3</sub> .	1.16416					
KHO.	1.2412	K <sub>2</sub> CO <sub>3</sub> .	1.3985	1.2073	Gain .1912 =	15.83

*Conclusions from the Results of Section A.*

1st. In nearly every instance with Acids and Alkalies, whether the electromotive force was measured by means of a positive metal of aluminium, tin, cadmium, zinc, or magnesium, there was a *loss* of that force due to the act of chemical union; and the proportion of losses to gains in the entire series was 81 to 1. 2nd. The amount of such loss depended upon five different conditions, viz. the kind of acid, of base, of positive metal, the degree of dilution, and to some extent the temperature. The losses were usually greater with all the other acids employed than with carbonic; they were larger with cæsia than with any other base; they were usually greater with aluminium than with any other positive metal, and with very weak solutions than with more concentrated ones; but the order of magnitude of loss with salts of potassium was nearly the same with strong solutions as with

weak ones. 3rd. The losses were often largest with the substances of greatest chemical energy, though several striking exceptions exist to this statement. Whilst they were usually larger with hydrochloric than with hydriodic acid, and with sulphuric than with nitric, chloric, carbonic, and the halogen acids, they were greater with formic acid than with either of these; and whilst they were larger with aluminium than with tin as a positive metal, they were usually larger with tin than with cadmium, and with cadmium than with zinc or magnesium. A reasonable explanation of the more feeble energy of union, and consequently smaller loss of energy, during the act of union of stronger substances than with weaker ones in certain cases is, that the energy of action and amount of loss depend upon the mutual relations of the inherent molecular motions of *each* of the two substances; that when these are so related that they cannot coexist, but must freely neutralize each other, the loss of energy is the greatest. The incompatible motions of carbon and oxygen, and the compatible ones of carbon and chlorine, at a red heat are familiar examples. 4th. The *order* of magnitude of loss of electromotive force was in the majority of cases substantially the same with different positive metals. 5th. In nearly all the cases in which thermochemical data are given, the loss of electromotive force varied directly as that of chemical heat, as if the two forms of energy were concomitant effects of the same cause, viz. decrease of molecular motion. And, 6th. The amount of loss did not vary regularly with the atomic weights. As the amounts of loss of electromotive force depend in every case upon *each* of the two uniting substances and upon the relations of their molecular motions to each other, it is not probable that they would vary regularly with the magnitude of the atomic weight of the positive ingredient alone in its chemical series, or with that of the negative one alone in its series, but would be affected by both. The general relations of the amounts of electromotive force of the ingredients and of their compounds in the various groups to the atomic weights of the substances, when measured by different positive metals, have already been partly examined (see Proc. Birm. Phil. Soc. 1891, vol. vii. p. 253). By arranging the series in each group in the order of the halogen acids, the agreement with the atomic weights was less conspicuous than when the order was that of the alkali metals.

The next section, "B," relates to the Formation of Salts from Acids and Carbonates, and gives in each instance the separate amounts of the electromotive force of the acid, of the carbonate, and of the salt produced by them, also the calcu-



lated mean amounts and the actual and percentage losses of that force due to the decomposition of the carbonates by the acid.

### Section B.—FORMATION OF SALTS FROM ACIDS AND CARBONATES.

TABLE IX.—*Positive metal, Aluminium.* Strong Solutions.

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
$\text{Ca}_2\text{CO}_3^*$	1·00388					
$\text{Rb}_2\text{CO}_3$	1·0096					
$\text{K}_2\text{CO}_3$	1·0239					
$\text{Na}_2\text{CO}_3$	1·0239					
HCl.	1·12986	$\text{CsCl}$	·9238	1·03028	Loss ·10648 =	10·33
		$\text{RbCl}$	1·0096	1·03850	„ ·0289	2·78
		$\text{KCl}$	1·0096	1·07070	„ ·0611	5·71
		$\text{NaCl}$	·9953	1·0670	„ ·0717	6·72
HBr.	1·0954	$\text{RbBr}$	1·9810	1·0450	Loss ·064 =	6·12
		$\text{KBr}$	1·0625	1·0382	„ ·0343	3·22
		$\text{NaBr}$	·95528	1·0664	„ ·11114	10·42
HI.	·9667	$\text{RbI}$	·8809	·9820	Loss ·1011 =	10·29
		$\text{KI}$	·9095	·9856	„ ·0791	8·02
		$\text{NaI}$	·89806	·9822	„ ·0841	8·56
$\text{H}_2\text{SO}_4$	1·08396	$\text{Ca}_2\text{SO}_4$	·92094	1·0244	Loss ·10346 =	10·09
		$\text{Rb}_2\text{SO}_4$	·9295	1·0318	„ ·1023	9·91
		$\text{K}_2\text{SO}_4$	·9238	1·0488	„ ·1250	11·90
		$\text{Na}_2\text{SO}_4$	·9181	1·0523	„ ·1342	12·75
$\text{HNO}_3$	1·0382	$\text{CsNO}_3$	·91236	1·0144	Loss ·10204 =	10·05
		$\text{RbNO}_3$	·91236	1·0198	„ ·10744	10·53
		$\text{KNO}_3$	·9095	1·0307	„ ·12120	11·75
		$\text{NaNO}_3$	·9095	1·0316	„ ·1221	11·85
$\text{HClO}_3$	1·0382	$\text{KClO}_3$	·88948	1·0317	Loss ·14222 =	13·78
		$\text{NaClO}_3$	·88948	1·0302	„ ·10302	13·06
Formic acid.	·7379	$\text{CsFormiate}$	·735104	·9476	Loss ·21256 =	22·43
		$\text{Rb}$ „	·74934	·9319	„ ·18256	19·57
		$\text{K}$ „	·7522	·9094	„ ·15720	17·28
		$\text{Na}$ „	·75506	·8910	„ ·13594	15·25

\* A specimen of caesium carbonate, containing silica, gave an electromotive force of only ·9924 volt.

TABLE X.—*Positive metal, Aluminium. Weak Solutions.*  
*Influence of Dilution.*

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
$K_2CO_3$ .	·8952					
HCl.	1·0096	KCl.	·9180	1·0676	Loss ·1496 =	14·0
HBr.	·9667	KBr.	·89234	·9338	„ ·04146	4·44
HI.	·86946	KI.	·85516	·8784	„ ·02324	2·64
$H_2SO_4$ .	1·0382	$K_2SO_4$ .	·87232	1·0733	Loss ·2010 =	18·72
$HNO_3$ .	·981	$KNO_3$ .	·85802	1·0423	Loss ·1843 =	17·68
Formic acid.	·7818	K Formiate.	·78080	·9717	Loss ·1909 =	19·68

TABLE XI.—*Positive metal, Tin. Strong Solutions.*

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
$Rb_2CO_3$ .	·6213					
$K_2CO_3$ .	·6178					
$Na_2CO_3$ .	·6178					
HCl.	·8066	RbCl.	·75512	·6660	Gain ·0891 =	13·37
		KCl.	·7494	·6831	„ ·0663	9·70
		NaCl.	·7351	·6947	„ ·0404	5·81
HBr.	·79802	RbBr.	·7351	·6943	Gain ·0408 =	5·87
		KBr.	·7494	·7662	Loss ·0168	2·19
		NaBr.	·73796	·72674	Gain ·01122	1·54
HI.	·73510	RbI.	·6779	·6812	Loss ·0033 =	·48
		KI.	·6893	·6940	„ ·0047	·67
		NaI.	·6922	·7008	„ ·0086	·12
$H_2SO_4$ .	·8209	$Rb_2SO_4$ .	·71794	·6809	Gain ·03704 =	5·44
		$K_2SO_4$ .	·71794	·7071	„ ·01084	1·53
		$Na_2SO_4$ .	·70364	·7153	Loss ·01166	1·63
$HNO_3$ .	·8352	$RbNO_3$ .	·68648	·6970	Loss ·0105 =	1·50
		$KNO_3$ .	·68632	·7215	„ ·03518	4·87
		$NaNO_3$ .	·68016	·7358	„ ·05564	7·56
$HClO_3$ .	·8123	$KClO_3$ .	·6636	·7201	Loss ·0565 =	7·84
		$NaClO_3$ .	·6636	·7373	„ ·0737	10·00
Formic acid.	·5492	Rb Formiate.	·4862	·6007	Loss ·1145 =	19·06
		K „	·492	·5903	„ ·0983	16·65
		Na „	·492	·5859	„ ·0939	16·03

TABLE XII.—*Positive metal, Cadmium.* Strong Solutions.

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Rb <sub>2</sub> CO <sub>3</sub> .	·8048					
K <sub>2</sub> CO <sub>3</sub> .	·78994					
Na <sub>2</sub> CO <sub>3</sub> .	·75848					
HCl.	1·1215	RbCl.	·93008	·8811	Gain ·04898 =	5·55
		KCl.	·98156	·8800	„ ·10156	11·54
		NaCl.	·99586	·9728	„ ·0232	2·38
HBr.	1·11026	RbBr.	·90434	·9310	Loss ·02666 =	2·86
		KBr.	·89560	·9629	„ ·0673	6·98
		NaBr.	·87860	1·0152	„ ·1366	13·45
HI.	1·0931	RbI.	·88432	·9566	Loss ·07228 =	7·55
		KI.	·88146	·9908	„ ·1093	11·03
		NaI.	·8786	1·0279	„ ·1493	14·56
H <sub>2</sub> SO <sub>4</sub> .	1·1646	Rb <sub>2</sub> SO <sub>4</sub> .	·94438	·9123	Gain ·0320 =	3·51
		K <sub>2</sub> SO <sub>4</sub> .	·9644	·9458	„ ·0186	2·0
		Na <sub>2</sub> SO <sub>4</sub> .	·9930	1·0115	Loss ·0185	1·82
HNO <sub>3</sub> .	1·1330	RbNO <sub>3</sub> .	1·01016	·9210	Gain ·0891 =	9·67
		KNO <sub>3</sub> .	1·0073	·9537	„ ·0536	5·63
		NaNO <sub>3</sub> .	·9844	1·0129	Loss ·02848	2·8
HClO <sub>3</sub> .	1·0645	KClO <sub>3</sub> .	·89004	·9410	Loss ·0510 =	5·42
		NaClO <sub>3</sub> .	·88146	·9895	„ ·10804	10·91
Formic acid.	·7356	Rb Formiate.	·6784	·7850	Loss ·1066 =	13·58
		K „	·6784	·7681	„ ·0897	11·67
		Na „	·68126	·8075	„ ·12624	15·64

TABLE XIII.—*Positive metal, Zinc.* Strong Solutions.

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Rb <sub>2</sub> CO <sub>3</sub> .	·8583					
K <sub>2</sub> CO <sub>3</sub> .	·74089					
Na <sub>2</sub> CO <sub>3</sub> .	·74089					
HCl.	1·46734	RbCl.	1·23082	1·0027	Gain ·2281 =	22·74
		KCl.	1·22710	·9922	„ ·2349	23·67
		NaCl.	1·25570	1·0382	„ ·2175	20·95
HBr.	1·3844	RbBr.	1·20708	1·0739	Gain ·13318 =	12·4
		KBr.	1·19850	1·0883	„ ·1102	10·12
		NaBr.	1·1842	1·1300	„ ·0542	4·79

Table XIII. (continued).

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HI.	1.3129	RbI.	1.1699	1.0963	Gain .0736 =	6.71
		KI.	1.16418	1.1125	" .05168	4.64
		NaI.	1.1413	1.1454	Loss .0041	3.59
H <sub>2</sub> SO <sub>4</sub> .	1.38726	Rb <sub>2</sub> SO <sub>4</sub> .	1.30146	1.0142	Gain .2872 =	28.30
		K <sub>2</sub> SO <sub>4</sub> .	1.29002	1.0092	" .2808	27.83
		Na <sub>2</sub> SO <sub>4</sub> .	1.2700	1.0514	" .2186	20.79
HNO <sub>3</sub> .	1.4720	RbNO <sub>3</sub> .	1.19278	1.0740	Gain .1187 =	11.05
		KNO <sub>3</sub> .	1.17848	1.0814	" .09708	8.97
		NaNO <sub>3</sub> .	1.1721	1.0370	" .1351	3.09
HClO <sub>3</sub> .	1.3558	KClO <sub>3</sub> .	1.1699	1.079	Gain .0009 =	8.42
		NaClO <sub>3</sub> .	1.19278	1.1188	" .0739	6.61
Formic acid.	1.0698	Rb Formiate.	1.04406	.9223	Gain .1217 =	13.20
		K "	1.04978	.8724	" .17738	20.33
		Na "	1.04092	.8936	" .1533	17.14

TABLE XIV.—Positive metal, Magnesium. Strong Solutions.

Ingredients.	E.M.F.	Compounds formed.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
K <sub>2</sub> CO <sub>3</sub> .	1.25836	K Formiate.	1.5558	1.4116	Gain .1442 =	10.21
Formic acid.	1.6416					
Acetic "	1.9592	K Acetate.	1.7131	1.5843	" .1288	8.13

*Conclusions from the Results in Section B.*

1st. In all the cases with acids and carbonates, whatever kind of positive metal was employed, there was either a loss or gain of electromotive force due to the chemical change. 2nd. The losses were more frequent than the gains. 3rd. Whilst in Section A, where the energy of chemical union was much greater, the number of cases of loss was 81, and of gain only 1, in the present Section the numbers were 57 and 13 respectively. 4th. The amount of loss or gain depended upon the same conditions as in Section A. 5th. The losses were greater with formic acid and with cæsia than with all other substances, the same as in Section A; and were usually larger with very dilute solutions than with more concentrated ones, but the order of loss with salts of potassium was nearly the same with strong solutions as with

weak ones, the same as in Section A. 6th. They were smaller with the carbonates than with the hydrates; whilst with aluminium as the positive metal, the losses with hydrates varied from 42·7 to 13·98 per cent., with the corresponding carbonates they varied from 22·43 to 2·78 per cent.; they were smaller with the carbonates, because the energy of chemical union was less, and because a portion of the energy had already been lost during the act of union of the base with the carbonic acid; the same circumstances explain to some extent the occurrence of gains instead of losses of electromotive force in some of the cases. And 7th. The magnitude of losses was largely affected by the kind of positive metal; whilst with aluminium the losses with carbonates varied from 22·43 to 2·78 per cent., with tin the variation was from a loss of 19·0 to a gain of 13·4 per cent.; the order of magnitude of loss, however, was in the majority of cases substantially the same with different positive metals. The proportion of gains to losses was much larger with zinc than with cadmium.

The next section, C, consists of Salts + Salts, and includes mixtures of substances, the ingredients of which, in most of the cases at least, are not usually considered to chemically unite with each other, and in which the energy of action is very feeble, and consequently the loss of electromotive force may be expected to be very much less than in Sections A and B. In this section, as in the previous ones, the ingredients of each pair are in equivalent proportions to each other, and the compounds are arranged in chemical series so as to facilitate comparison with the atomic weights, &c. of the metallic bases.

## Section C.—SALTS + SALTS.

TABLE XV.—*Positive metal, Cadmium. Strong Solutions.*

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
KCl	·97870					
CaCl <sub>2</sub>	·96154	2KCl + CaCl <sub>2</sub>	·9501	·9713	Loss ·0212	= 2·18
SrCl <sub>2</sub>	·96440	" + SrCl <sub>2</sub>	·9501	·9713	" ·0212	2·18
BaCl <sub>2</sub>	·97298	" + BaCl <sub>2</sub>	·94152	·9753	" ·0337	3·46
MgCl <sub>2</sub>	·96726	2KCl + MgCl <sub>2</sub>	·9501	·9742	Loss ·0241	= 2·47
ZnCl <sub>2</sub>	·96726	" + ZnCl <sub>2</sub>	·95727	·9732	" ·0159	1·63
CdCl <sub>2</sub>	·96440	" + CdCl <sub>2</sub>	·9358	·9708	" ·0350	3·60
K <sub>2</sub> SO <sub>4</sub>	·96440					
MgSO <sub>4</sub>	·96154	K <sub>2</sub> SO <sub>4</sub> + MgSO <sub>4</sub>	·95296	·9625	Loss ·0095	= ·99
ZnSO <sub>4</sub>	·97298	" + ZnSO <sub>4</sub>	·95382	·9685	" ·0147	1·51
CdSO <sub>4</sub>	·97870	" + CdSO <sub>4</sub>	·95382	·9722	" ·0184	1·89

Table XV. (continued).

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
NaCl.	·99586	2NaCl + CaCl <sub>2</sub> .	·97298	·9791	Loss ·006	= ·61
		" + SrCl <sub>2</sub> .	·97298	·9778	" ·0048	·49
		" + BaCl <sub>2</sub> .	·9787	·9812	" ·0025	·25
		2NaCl + MgCl <sub>2</sub> .	·9787	·9830	Loss ·0043	= ·43
		" + ZnCl <sub>2</sub> .	·9787	·9804	" ·0017	·17
		" + CdCl <sub>2</sub> .	·97584	·9766	" ·0008	·08
		2NaCl + MgSO <sub>4</sub> .	·9787	·9785	Gain ·0002	= ·02
		" + ZnSO <sub>4</sub> .	·98156	·9826	Loss ·001	·10
		" + CdSO <sub>4</sub> .	·98442	·9848	" ·0004	·04
Na <sub>2</sub> SO <sub>4</sub> .	·9930	Na <sub>2</sub> SO <sub>4</sub> + 2KCl.	·98442	·9855	Loss ·0011	= ·11
AmCl.	·90148	" + 2NaCl.	·9930	·9942	" ·0012	·12
		" + 2AmCl.	·9501	·9536	" ·0025	·36
		Na <sub>2</sub> SO <sub>4</sub> + MgSO <sub>4</sub> .	·97584	·9785	Loss ·0027	= ·27
		" + ZnSO <sub>4</sub> .	·97870	·9823	" ·0036	·36
		" + CdSO <sub>4</sub> .	·98156	·9845	" ·0029	·29
Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .	·8214	4KCl + Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> .	·89862	·9039	Loss ·00528	= ·58
K <sub>2</sub> CO <sub>3</sub> .	·78994					
Na <sub>2</sub> CO <sub>3</sub> .	·75848	K <sub>2</sub> CO <sub>3</sub> + Na <sub>2</sub> CO <sub>3</sub> .	·77564	·7762	Loss ·0005	= ·064
KHO.	·8843	KHO + KCl.	·9072	·9417	Loss ·0345	= 3·67

*Influence of Temperature.*

The mixture  $\text{Na}_2\text{SO}_4 + 2\text{KCl}$  in the above table was re-examined with each of the three solutions at about  $98^\circ\text{C}$ . The electromotive force of the KCl solution was ·9501, of the  $\text{Na}_2\text{SO}_4$  ·9644; and of the mixture of the two ·95382; the calculated electromotive force of the latter was ·9570, and the loss ·00348 or ·363 per cent. The rise of temperature therefore, whilst diminishing somewhat the electromotive force of each of the three liquids, had very little effect upon the percentage of loss in this case.

TABLE XVI.—Positive metal, Zinc.

Strength of Solution 1 equivalent weight in grains in 31,000 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
KCl.	1·295					
KNO <sub>3</sub> .	1·14988	KCl + KNO <sub>3</sub> .	1·1413	1·2116	Loss ·0703	= 5·82

The following remarks may be made respecting the results in Section C:—1st. In all the twenty-six instances, except one of Table XV., there is a loss of electromotive force. 2nd. The amounts of change of that force are all very small. 3rd. They are much smaller than those obtained with the same positive metal in Sections A and B, where chemical action is much more energetic. If we compare them with those in Tables IV. and XII., we find that whilst the changes in Section C vary only from a maximum loss of 3·6 to a gain of ·02 per cent., in Table IV. the losses vary from 19·2 to 10·65 per cent., and in Table XII. the amount of change is from a loss of 15·64 to a gain of 11·54 per cent. And, 4th, the results show that the method of measurement is sufficiently delicate to be employed with mixtures of neutral salts which are not considered usually to act chemically upon each other.

## Section D.—ACIDS + SALTS.

TABLE XVII.—Positive metal, Cadmium. Strong Solutions.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HCl	1·1217					
CsCl	·93866	HCl + CsCl	1·07308	·9713	Gain ·10178 = 10·47	
RbCl	·93008	" + RbCl	1·04734	·9747	" ·0726 7·47	
KCl	·98156	" + KCl	1·03590	1·0276	" ·0083 ·907	
NaCl	·99586	" + NaCl	1·02732	1·0442	Loss ·0169 1·616	
BaCl <sub>2</sub>	·97298	2HCl + BaCl <sub>2</sub>	1·05878	0·0116	Gain ·0472 = 4·666	
SrCl <sub>2</sub>	·96440	" + SrCl <sub>2</sub>	1·05592	0·0140	" ·0419 4·136	
CaCl <sub>2</sub>	·95868	" + CaCl <sub>2</sub>	1·05020	0·0233	" ·0269 2·648	
MgCl <sub>2</sub>	·96726	2HCl + MgCl <sub>2</sub>	1·04448	1·3333	Gain ·0112 = 1·083	
ZnCl <sub>2</sub>	·96726	" + ZnCl <sub>2</sub>	1·05592	1·0212	" ·03472 3·40	
CdCl <sub>2</sub>	·9644	" + CdCl <sub>2</sub>	1·06164	1·0092	" ·06072 6·016	
HBr	1·11026					
RbBr	·90434	HBr + RbBr	1·08452	·9721	Gain ·1124 = 11·56	
KBr	·89516	" + KBr	1·05306	·9822	" ·0707 7·19	
NaBr	·87860	" + NaBr	1·07880	·9800	" ·0988 10·08	
H <sub>2</sub> SO <sub>4</sub>	1·1646					
Rb <sub>2</sub> SO <sub>4</sub>	·94438	H <sub>2</sub> SO <sub>4</sub> + Rb <sub>2</sub> SO <sub>4</sub>	1·08452	1·0036	Gain ·0809 = 8·061	
K <sub>2</sub> SO <sub>4</sub>	·9644	" + K <sub>2</sub> SO <sub>4</sub>	1·10168	1·0365	" ·0651 6·287	
Na <sub>2</sub> SO <sub>4</sub>	·9930	" + Na <sub>2</sub> SO <sub>4</sub>	1·1074	1·1216	Loss ·0142 1·266	
Am <sub>2</sub> SO <sub>4</sub>	·9601	" + Am <sub>2</sub> SO <sub>4</sub>	1·0645	1·0415	Gain ·023 2·20	
MgSO <sub>4</sub>	·9644	H <sub>2</sub> SO <sub>4</sub> + MgSO <sub>4</sub>	1·07594	1·0544	Gain ·0215 = 2·039	
ZnSO <sub>4</sub>	·9787	" + ZnSO <sub>4</sub>	1·08452	1·0490	" ·03552 3·386	
CdSO <sub>4</sub>	·9673	" + CdSO <sub>4</sub>	1·08166	1·0030	" ·07866 7·842	
		2HCl + Rb <sub>2</sub> SO <sub>4</sub>	1·0931	·9825	Gain ·1106 = 11·25	
		H <sub>2</sub> SO <sub>4</sub> + CdCl <sub>2</sub>	1·09024	1·0342	" ·056 5·41	
HNO <sub>3</sub>	1·13314	2HNO <sub>3</sub> + Rb <sub>2</sub> SO <sub>4</sub>	1·09024	1·0050	" ·0852 8·47	
Citric acid.	1·08166	Citric acid + 3KCl	1·08164	1·0262	" ·0554 3·45	

TABLE XVIII.—*Positive metal, Zinc.*

Strength of Solution 1 equivalent weight in grains in 31,000 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
H <sub>2</sub> CrO <sub>4</sub> .	1.4988					
K <sub>2</sub> SO <sub>4</sub> .	1.2843	H <sub>2</sub> CrO <sub>4</sub> +K <sub>2</sub> SO <sub>4</sub> .	1.4416	1.3711	Gain .0705 =	5.14

*Conclusions from Results of Section D.*

1st. A sufficient number and variety of instances of what are generally considered to be mere mechanical mixtures are here given to show that such cases are attended some by a loss and others by a gain of energy. 2nd. The gains were more frequent than the losses in the proportion of 23 to 2, and were of greater magnitude. Whilst with cadmium in Table XII. of Section B, where the energy of chemical union was much larger, the number of cases of loss was 14 and gain 6, in this section the numbers were 2 and 22 respectively; and whilst in the cadmium table of the former section, the largest loss was 15.64 per cent., in this one it was only 1.6 per cent.; in this section there was no case of large loss because there was none of strong chemical union. And 3rd. In this series, as in Sections A and B, the order of magnitude of the results appears to agree with that of the magnitudes of the atomic weights of the metallic bases.

Section E.—ACIDS + ACIDS.

TABLE XIX.—*Positive metal, Zinc.*

Strength of Solution 1 equivalent weight in grains in 31,000 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HCl.	1.41014	H <sub>2</sub> SO <sub>4</sub> +2HCl.	1.41014	1.4117	Loss .0015	1.06
H <sub>2</sub> SO <sub>4</sub> .	1.41300	" +2HNO <sub>3</sub> .	1.3924	1.3969	" .0045	.322
HNO <sub>3</sub> .	1.3844	Citric acid+3HCl.	1.3924	1.3864	Gain .0060	.43
Citric acid.	1.37296	2 " " +3H <sub>2</sub> SO <sub>4</sub> .	1.3924	1.3903	" .0021	.15
Formic "	1.21566	Formic " +HCl.	1.31576	1.3015	" .0142	1.09
		2 " " +H <sub>2</sub> SO <sub>4</sub> .	1.3129	1.3174	Loss .0045	.34
H <sub>2</sub> CrO <sub>4</sub> .	1.4988	3H <sub>2</sub> CrO <sub>4</sub> +2 Citric acid.	1.4845	1.4333	Gain .0512	3.57
Oxalic acid.	1.3701	Oxalic acid +H <sub>2</sub> SO <sub>4</sub> .	1.3844	1.3924	Loss .008	.57



TABLE XX.—*Positive metal, Magnesium.*

Strength of Solution same as in Table XIX.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HCl.	2.0134					
H <sub>2</sub> SO <sub>4</sub> .	2.0162	H <sub>2</sub> SO <sub>4</sub> +2HCl.	2.0162	2.0150	Gain .0012	= .06
HNO <sub>3</sub> .	1.9848	" + 2HNO <sub>3</sub> .	2.00196	1.9985	" .00346	.17
Formic acid	1.6130	Formic acid + HCl.	1.8990	1.7901	" .109	6.09
		2 " + H <sub>2</sub> SO <sub>4</sub> .	1.90186	1.8200	" .0818	4.49
Oxalic acid.	1.7274	H <sub>2</sub> SO <sub>4</sub> +Oxalic acid.	1.93046	1.8780	" .05246	2.79

The amounts of change of energy in these experiments are all very small, as in the experiments with Salts + Salts, and the general conclusions to be drawn from the results are largely similar to those in Section D. In the present section, as in some others, the gains of energy are more frequent and larger with a positive metal composed of magnesium than with one of zinc.

## Section F.—ALKALIES + ALKALIMS.

TABLE XXI.—*Positive metal, Aluminium.*

Strength of Solution 1 equivalent weight in grains in 1800 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
KHO.	1.3814					
NaHO.	1.3914	KHO+NaHO.	1.3871	1.3855	Gain .0016	= .11

## Section G.—HALOGENS + HALOGENS.

TABLE XXII.—*Positive metal, Zinc.*

Strength of Solution 1 equivalent weight in grains in 511,500 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl	1.9250	Cl+Br.	1.8992	1.8873	Gain .0119	= .63
Br.	1.8706	Cl+I.	1.7133	1.5471	" .1662	10.74
I.	1.4416	Br+I.	1.69328	1.6074	" .0859	5.33

## Section H.—HALOGENS + ACIDS.

TABLE XXIII.—*Positive metal, Zinc.*

Strength of Solution same as in Table XXII.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl.	1·9250					
HCl.	1·3558	Cl + HCl.	1·76478	1·6364	Gain ·12838 = 7·84	
H <sub>2</sub> SO <sub>4</sub> .	1·33578	Cl + H <sub>2</sub> SO <sub>4</sub> .	1·77622	1·5833	„ ·19292 12·18	
Br.	1·8706	Br + HCl.	1·79338	1·7093	Gain ·084 = 4·91	
		2Br + H <sub>2</sub> SO <sub>4</sub> .	1·78480	1·6674	„ ·1174 7·042	
Formic acid.	1·27858	Cl + Formic acid.	1·80482	1·5601	Gain ·24472 = 15·68	
I.	1·4416					
Citric acid.	1·24098	3I + Citric acid.	1·3987	1·3773	Gain ·0214 = 1·53	

## Section I.—HALOGENS + SALTS.

TABLE XXIV.—*Positive metal, Zinc.*

Strength same as in Table XXII.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl.	1·9250					
Br.	1·8706	Cl + KCl.	1·8134	1·4290	Gain ·3844 = 26·9	
I.	1·4416	Br + KCl.	1·69328	1·5437	„ ·1495 9·684	
KCl.	1·1927	I + KCl.	1·3558	1·3500	„ ·0058 ·43	
KBr.	1·1556	Br + KBr.	1·7333	1·443	Gain ·2904 = 20·12	
KI.	1·14702	I + KI.	1·2929	1·2747	„ ·0181 1·42	
KNO <sub>3</sub> .	1·13844	Br + KNO <sub>3</sub> .	1·79338	1·4620	Gain ·3313 = 22·66	
		I + KNO <sub>3</sub> .	1·3558	1·3072	„ ·0486 ·371	
KMnO <sub>4</sub> .	1·3844	Br + KMnO <sub>4</sub> .	1·8134	1·5474	Gain ·266 = 17·18	
		I + KMnO <sub>4</sub> .	1·4158	1·4098	„ ·006 ·42	
ZnSO <sub>4</sub> .	1·13558	2Br + ZnSO <sub>4</sub> .	1·7562	1·5019	Gain ·2543 = 16·93	
		2I + ZnSO <sub>4</sub> .	1·3415	1·3228	„ ·0187 1·41	
K <sub>2</sub> CO <sub>3</sub> .	1·0898	Cl + K <sub>2</sub> CO <sub>3</sub> .	1·6704	1·3735	Gain ·2969 = 21·61	

TABLE XXV.—*Positive metal, Magnesium.*

Strength of Solution 1 equivalent weight in grains in 5115 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br.	2.2565					
EbCl.	1.58726	Br+KCl.	2.1850	1.8604	Gain .3246 =	17.45

The solutions used in this case were 100 times stronger than in Tables XXII., XXIII., and XXIV. The electromotive force in so strong a solution was very variable.

In all the cases of Sections F, G, H, and I only *gains* of energy occurred. The largest gain was 27.0 per cent. The amount of gain usually varied inversely as the atomic weight of the halogens.

## Section J.—HALOGENS + ALKALIES. STRONG SOLUTIONS.

*Effect of Heating.*TABLE XXVI.—*Positive metal, Aluminium.*

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br.	1.5816					
KHO.	1.3814	Br+KHO.	1.5241	1.4991	Gain .0250=	1.66
After heating 1 minute to above 90° C. and cooling.						
		Br+KHO.	1.5101	1.4991	Gain .0110=	.73

The amount of change produced by heat was = a loss of about .93 per cent.

TABLE XXVII.—*Positive metal, Tin.*

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br.	1.2213					
KHO.	.9210	Br+KHO.	.9496	1.0976	Loss .1480=	13.48
After heating 1 minute to above 90° C. and cooling.						
		Br+KHO.	.9067	1.0976	Loss .1909=	17.40

The amount of change produced by heat was = a loss of 3.92 per cent. The electromotive force with aluminium and with tin in the mixture of  $\text{Br} + \text{KHO}$  was rather variable.

TABLE XXVIII.—*Positive metal, Zinc.*

Strength of Solution 1 equivalent weight in grains in  
511,500 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl. KHO.	1.9250 1.07552	Cl + KHO.	1.8420	1.4055	Gain .4365	= 31.06
After heating 65 minutes to 98° C. and cooling.						
		Cl + KHO.	1.1327	1.4055	Loss .2728	= 19.40
Br.	1.8706	Br + KHO.	1.60614	1.4696	Gain .2654	= 15.41
After heating 65 minutes to 98° C. and cooling.						
		Br + KHO.	1.1270	1.4696	Loss .3426	= 23.31
I.	1.4416	I + KHO.	1.3844	1.3295	Gain .0549	= 4.136
After heating 35 minutes to 98° C. and cooling.						
		I + KHO.	1.1270	1.3295	Loss .2025	= 15.23

In each of these cases the process of heating converted a gain into a loss, thus indicating chemical change. The amount of change produced by heat in these three cases was = 50.46, 38.72, and 19.37 per cent. of loss respectively, and varied inversely as the atomic weights of the halogens. In Table XXVIII. the amount of original gain varied inversely as the atomic weights of the halogens, the same as in Sections F, G, H, and I. Whether the mixtures were permanently affected by light, or were spontaneously unstable and changed by mere lapse of time, was not ascertained. Probably some of the mixtures in Sections G, H, and I were also changeable by heat.

The results given in this Section and in the following one show that the method can be employed for measuring the relative amounts of change of energy caused by heating electrolytes.

In the following experiments the effect of heating aqueous solutions of the halogens alone is shown :—

## Section K.—EFFECT OF HEATING AQUEOUS SOLUTIONS OF THE HALOGENS.

TABLE XXIX.—Positive metal, Cadmium.

Strength of Solution 1 equivalent weight in grains in 449,500 grains of water.

Ingredients.	E.M.F.	Mixture.	E.M.F.
Water at 18° C.	·850	Water + Cl at 10° C.	1·6508
After heating to 90° C. during 5 minutes and cooling.			1·61076
" " "		5 " "	1·5650
" " "		5 " "	" "
" " "		15 " "	1·5078
" " "		15 " "	" "
" " "		30 " "	" "

There still remained an odour of chlorine, and the liquid liberated iodine from potassium iodide after heating. The loss of electromotive force was about 8·6 per cent.

	Mixture.	E.M.F.
	Water + Br at 9·5 C.	1·5135
After heating to 90° C. during 5 minutes and cooling.		1·50208
" " "	5 " "	1·48492
" " "	5 " "	1·4220
" " "	15 " "	1·0902
" " "	15 " "	·993

The liquid was now colourless and odourless, and showed no acid reaction with test-paper. The loss of electromotive force was about 34·35 per cent. The last amount of electromotive force was slightly larger than that obtained with dilute hydrobromic acid of equivalent strength.

	Mixture.	E.M.F.
	Water + I at 10° C.	1·1646
After heating to 90° C. during 5 minutes and cooling.		1·14458
" " "	5 " "	" "
" " "	5 " "	" "
" " "	15 " "	" "
" " "	15 " "	" "

The degree of colour of the liquid was diminished about 50 per cent. The loss of electromotive force was about 1·72 per cent.

In each of these three cases a loss of electromotive force  
*Phil. Mag.* S. 5. Vol. 33. No. 200. Jan. 1892. E

was produced by heating and then cooling the liquid, and was greatest with bromine and least with iodine.

The electromotive force at 17° C., in a solution of 35.5 grains of chlorine in 511,500 grains of water, of a voltaic couple of magnesium and platinum was 2.6124, and of aluminium and platinum 1.553 volt.

*Relations of Electromotive Force to Dilution and Specific Gravity of Electrolytes.*

In a previous research on "Relation of Volta Electromotive Force to Latent Heat, Specific Gravity, &c. of Electrolytes" (Philosophical Magazine, August 1891, p. 157), the results obtained by diluting about twenty different liquids showed an increase of mean amount of electromotive force in nearly all cases; and that if the amounts of such change were arranged in the order of their respective magnitudes, all the strong acids were at one end of the series, all the alkalies at the other, and the neutral salts in the middle, thus forming a kind of volta-tension series. Dilution of strong solutions of acids largely increased, and of those of alkalies only feebly increased, the mean amounts of their volta-electromotive force.

With regard to any relation of volta-electromotive force to specific gravity, in cases of *chemical union*, various investigators have already shown that contraction of total volume of the ingredients nearly always occurs, and that it is usually attended by evolution or loss of heat; and the results of the present research show that these effects are very generally accompanied by *decrease* of mean amount of electromotive force. But in cases of mere *dilution*, the increase of mean specific gravity which usually takes place is nearly always attended by *increase* of mean electromotive force.

REMARKS AND CONCLUSIONS.

The following are the chief results obtained in this research:—1st. In every instance either a loss or gain of electromotive force occurred during the mixing of any two electrolytes. 2nd. The amount of loss or gain differed in every different case, and depended upon the nature of each of the constituents of the mixture, the kind of positive metal, and the degree of concentration and temperature of the liquid. 3rd. The loss or gain of mean amount of electromotive force coincided with the presence or absence of chemical change. The amounts of loss and the proportion of number of cases of loss are largest in Section A, in which the degree of chemical action is the greatest, and in Section J,

where chemical change by heating occurred. The gains are largest and most frequent in those mixtures in which no recognized chemical change took place, and in which an acid or halogen existed in a free state to act strongly upon the positive metal, as in Sections H, I, and J. 4th. In cases of *chemical union*, increase of mean specific gravity of the uniting substances was usually attended by *decrease* of mean electromotive force, and in those of mere *dilution* it was accompanied by *increase* of mean electromotive force of the ingredients. 5th. In certain cases heating the liquid permanently altered the amount of change of energy, and converted a gain into a loss, evidently because it produced chemical change. These instances may be viewed as ones of unstable mixture, the chemical equilibria of which are permanently upset by elevation of temperature, and the molecular changes of which are not reversible. 6th. As action and reaction are always equal and contrary, we may conclude that the losses of energy suffered by the two mutually reacting substances are always equal in amount; this remark would apply equally to the two soluble substances during the act of mixing, and to the positive metal and the substance which acts upon it. And 7th. As the whole of the cases of change of mean amount of electromotive force in this research may be arranged in an unbroken series, beginning with those of strongest chemical action and ending with those of simple physical mixture and dilution, and as the relative amount of change of mean electromotive force in this series varies by insensible degrees from a large percentage of loss to a considerable one of gain, we may conclude that essentially the same fundamental kind of energy operates in all the cases; and the entire order and its energy may be compared with those of a volta-tension series of metals.

The results in general indicate the existence of an extensive system of quantitative relations between voltaic electromotive force and the atomic weights of the positive metals and of the negative and positive constituents of the compounds acting upon them; and largely also between the losses of electromotive force and the amount of chemical heat; the latter is already known to a considerable extent. With the zinc series of positive metals the electromotive force was usually greater the smaller the atomic weight of the positive metal and of that of the halogen, of the acid or salt, and the larger that of the metallic base of the salt. With the halogens and their acids it was greater the smaller the atomic weight of the halogen. With the alkali salts of the halogens it was larger the smaller the atomic weight of the halogen and the greater that of the

alkali metal ; but with the halogen salts of the calcium and magnesium group of metals, and with oxygen salts of the alkali metals, the influence of the atomic weight of the metal was less manifest. (See also "Some Relations of Electromotive Force to Atomic Weight" &c., Proc. Birm. Phil. Soc. 1891, vol. vii. part 2, p. 253.)

I beg to offer the following simple explanation of the chief result, viz. that the loss or gain of mean amount of electromotive force coincided with the presence and absence of chemical action. The electromotive force appears to depend essentially upon the degree of freedom of molecular motion. The substance which most strongly attacks the positive metal, and by neutralizing some of its molecular motion excites electromotive force, is the most electronegative constituent of the liquid. When this substance (acid or halogen) *chemically combines* with any ingredient of the mixture it usually loses heat and energy freely ; by this act of union its molecules acquire less freedom of motion, and consequently can only excite a *decreased* mean amount of electromotive force with the electropositive metal. But when the solution of this substance is only *diluted* by the second liquid, a much less amount of its molecular motion is neutralized or lost, and the molecules of the substance acquire by the dilution a larger sphere of action and an increased degree of freedom of motion, which usually more than compensates the small amount of loss of energy and of contraction of total volume of the two liquids, so that the molecules of the substance can now excite an *increased* mean amount of electromotive force. These remarks must apply in some degree to the oxygen of the water, because the water itself excites some degree of volta-electromotive force.

All the results obtained appear to be consistent with a kinetic theory of chemical action, and the magnitudes of the amounts of electromotive force obtained appear to be determined by the amount of incompatible molecular motions of the mutually acting positive metal and the electronegative constituent of the liquid. As the amounts of action and reaction are equal, the degree of energy excited, both between the two liquids on mixing, and between the positive metal and the liquids before mixing and after, must be limited by the amount of incompatible molecular motion ; the greater the amount of such motion in the two liquids before mixing the larger the quantity of energy lost by neutralization of those motions during mixing, and the less the total amount of energy left in the liquid substances. According to these views, voltaic electromotive force is directly proportional to the degree of freedom of the incompatible molecular motions



of the electropositive metal and of the electronegative acid or halogen of the liquid.

We may regard every instance of chemical union, mixture, or dilution in this research as a case of balance and change of molecular motion of all the substances composing the liquid in the particular case. *Previous to mixing*, the molecular movements of the liquid are mutually compatible, and therefore coexist without neutralizing one another: they are in a balanced condition, the liquid is in a state of "rest," and no heat or other form of energy is being evolved or absorbed. *During mixing*, a more or less profound change and redistribution of the movements takes place, those portions of them in the two liquids which are mutually incompatible neutralize one another, heat is either evolved or absorbed, contraction or expansion of the total volume of liquid occurs, and a change of the mean amount of those portions of molecular motion of the liquid, which are incompatible with some of the molecular motions of the positive metal, takes place.

The amount of each of these several alterations differs in every different case; in cases of *chemical union* there nearly always occur contraction of volume, evolution of heat, and *decrease* of the mean amount of incompatible molecular motion in relation to that of the positive metal, but in those of *simple dilution* an *increase* of the latter effect very usually takes place. *After mixing*, a new state of balance of molecular motion occurs, and the amount of change which has happened, and the point or state of balance attained, depend upon the various conditions already mentioned. In a few cases, a temporary or unstable intermediate state of balance occurs, and the more fixed or final condition is only attained on the application of heat &c. (see Sections J and K). Immersion of the positive metal and closing the electric circuit introduce new conditions, which again disturb the balance.

*Applications of the Method.*—The examples given show that the method is applicable to the examination of a large variety of chemical and physical changes in dissolved electrolytic substances, including cases of chemical union and decomposition by whatever causes determined; simple physical mixture and dilution; the investigation of the relations of voltaic electromotive force to temperature, specific gravity, atomic weight, amount of chemical heat, &c., and that it is capable of detecting small amounts of molecular change in electrolytes, such as those which occur when neutral salts are dissolved together without any manifest chemical action.

IV. *On the Connexion between Recurring Formulæ involving Sums of Divisors and the Corresponding Formulæ involving Differences between Sums of Even and Uneven Divisors.* By J. W. L. GLAISHER, *Sc.D., F.R.S.\**

§ 1. **O**F all the numerous recurring formulæ relating to the divisors of numbers perhaps the simplest is

$$\zeta(n) + \zeta(n-1) + \zeta(n-3) + \zeta(n-6) + \zeta(n-10) + \&c. = 0 \dagger,$$

where  $\zeta(n)$  denotes the excess of the sum of the uneven divisors of  $n$  above the sum of the even divisors (this excess being of course negative when  $n$  is even); and  $\zeta(0)$ , which occurs when  $n$  is a triangular number, is to have the conventional value  $-n$ .

This theorem asserts that,  $n$  being any number, the sum of the uneven divisors of  $n$ ,  $n-1$ ,  $n-3$ , &c. is equal to the sum of the even divisors of these same numbers, if  $n$  is not a triangular number; and that when  $n$  is a triangular number, the former sum exceeds the latter sum by  $n$ .

For example, let  $n=9$ , which is not a triangular number. The uneven divisors of 9, 8, 6, 3 are 1, 3, 9; 1; 1, 3; 1, 3, the sum of which is 22. The even divisors of the same numbers are 2, 4, 8; 2, 6, the sum of which is also 22.

As another example let  $n=10$ , which is a triangular number. The uneven divisors of 10, 9, 7, 4 are 1, 5; 1, 3, 9; 1, 7; 1, the sum of which is 28. The even divisors are 2, 10; 2, 4, the sum of which is 18. The excess of the former sum over the latter sum is therefore equal to  $n$ .

§ 2. The corresponding formula (*i. e.* the formula having the same arguments) which relates to the sums of divisors is  $\sigma(n) - 3\sigma(n-1) + 5\sigma(n-3) - 7\sigma(n-6) + 9\sigma(n-10) - \&c. = 0 \dagger$ , where  $\sigma(n)$  denotes the sum of all the divisors of  $n$ , and  $\sigma(0)$  when it occurs, is to have the value  $\frac{1}{2}n$ .

§ 3. The object of this note is to point out that the two formulæ are derivable from a single general theorem relating to the actual divisors of the numbers  $n$ ,  $n-1$ ,  $n-3$ , &c. It is especially interesting to notice how it comes about that the coefficients are 1,  $-3$ ,  $5$ ,  $-7$ , &c. in the one case and that they are all unity in the other.

§ 4. The general theorem may be stated as follows:—Let  $G_r\{\phi(d), \psi(d), \dots\}$  denote the group of numbers

\* Communicated by the Author.

† Proc. Lond. Math. Soc. vol. xv. (1884) p. 110; or Proc. Camb. Phil. Soc. vol. v. (1884) p. 116.

‡ Quart. Journ. Math. vol. xix. (1883) p. 220; or Proc. Camb. Phil. Soc. vol. v. (1884) p. 109.

$$\phi(1), \phi(d_1), \phi(d_2), \dots, \phi(d_f),$$

$$\psi(1), \psi(d_1), \psi(d_2), \dots, \psi(d_f),$$

where  $1, d_1, d_2, \dots, d_f$  are all the divisors of  $r$ , the suffix of  $G$ ; then the numbers given by the formula

$$G_n(d) - G_{n-1}(d, d \pm 1) + G_{n-2}(d, d \pm 1, d \pm 2) \\ - G_{n-3}(d, d \pm 1, d \pm 2, d \pm 3) + \&c.$$

all cancel each other if  $n$  is not a triangular number; but when  $n$  is a triangular number,  $\frac{1}{2}g(g+1)$ , there remain uncanceled

one 1, two 2's, three 3's, ...,  $g$   $g$ 's,

these numbers having the positive or negative sign according as  $g$  is uneven or even.

§ 5. As an example of this theorem, let  $n=9$ . We write down in a central line the divisors of 9, 8, 6, and 3. In the line above, beginning with the divisors of 8, we write the numbers obtained by adding unity to the divisors, and in the line below the numbers obtained by subtracting unity from the divisors: in the second line above, beginning with the divisors of the next number, 6, we write the numbers obtained by adding 2 to the divisors, and, in the second line below, the numbers obtained by subtracting 2, and so on. The scheme of numbers thus formed is

$$\begin{array}{rcccc} & & & & 4, 6 \\ & & & & 3, 4, 5, 8 & 3, 5 \\ & & & 2, 3, 5, 9 & 2, 3, 4, 7 & 2, 4 \\ 1, 3, 9; & 1, 2, 4, 8; & 1, 2, 3, 6; & & 1, 3. \\ & 0, 1, 3, 7 & 0, 1, 2, 5 & & 0, 2 \\ & & -1, 0, 1, 4 & & -1, 1 \\ & & & & -2, 0 \end{array}$$

We then change the signs of all the numbers in the second and fourth groups, thus finally obtaining the system of numbers

$$\begin{array}{rcccc} & & & & -4, -6 \\ & & & & 3, 4, 5, 8, -3, -5 \\ & & -2, -3, -5, -9, 2, 3, 4, 7, & -2, -4 \\ 1, 3, 9, & -1, -2, -4, -8, 1, 2, 3, 6, & -1, -3, \\ & 0, -1, -3, -7, 0, 1, 2, 5, & 0, -2 \\ & -1, 0, 1, 4, & 1, -1 \\ & & 2, 0 \end{array}$$

all of which cancel one another; *i. e.* there are five 1's and five (-1)'s, four 2's and four (-2)'s, four 3's and four (-3)'s, three 4's and three (-4)'s, two 5's and two (-5)'s, one 6 and one -6, one 7 and one -7, one 8 and one -8, one 9 and one -9.

§ 6. As a second example let  $n=10$ , so that  $g$  is 4. We form, as before, the groups

			4,	5,	7
		3, 9	3,	4,	6
	2, 4, 10	2, 8	2,	3,	5
1, 2, 5, 10;	1, 3, 9;	1, 7;	1,	2,	4,
	0, 2, 8	0, 6	0,	1,	3
		-1, 5	-1,	0,	2
			-2,	-1,	1

and, changing the signs in the second and fourth groups, we obtain the numbers

			-4,	-5,	-7
		3, 9,	-3,	-4,	-6
	-2, -4,	-10, 2, 8,	-2,	-3,	-5
1, 2, 5, 10,	-1, -3,	-9, 1, 7,	-1,	-2,	-4,
	0, -2,	-8, 0, 6,	0,	-1,	-3
		-1, 5,	1,	0,	-2
			2,	1,	-1

all of which cancel one another except one -1, two (-2)'s, three (-3)'s, and four (-4)'s.

§ 7. In the general theorem the actual divisors, and numbers formed from them, cancel one another (with certain exceptions when  $n$  is a triangular number). We may therefore replace these divisors and numbers by any functions of themselves, the functions being the same for all and changing sign with the arguments: and we may further combine these functions by addition, thus obtaining numerical theorems which connect together functions of the divisors of the numbers  $n, n-1, n-3$ , &c.

§ 8. The simplest method of deducing a numerical formula from the general theorem is merely to add together all the numbers in each of the groups. It is evident that the sum of the numbers in the first group is the sum of the divisors of  $n$ . In the second group the sum of the numbers is equal to three times the sum of the divisors of  $n-1$ ; for,  $d$  being any divisor of  $n-1$ , the numbers in the upper line are of the

form  $d+1$ , and those in the lower line of the form  $d-1$ , so that the sum of the three lines is  $3\Sigma d$ . In the third group the sum of the numbers is five times the sum of the divisors of  $n-3$ ; and so on.

We thus obtain as result that

$\sigma(n) - 3\sigma(n-1) + 5\sigma(n-3) - 7\sigma(n-6) + 9\sigma(n-10) - \&c.$   
is equal to zero if  $n$  is not a triangular number, and is equal to

$$(-1)^{s-1}(1^2 + 2^2 + 3^2 + \dots + g^2),$$

when  $n$  is the triangular number  $\frac{1}{2}g(g+1)$ .

We know that

$$1^2 + 2^2 + 3^2 + \dots + g^2 = \frac{1}{6}g(g+1)(2g+1);$$

and since the coefficient of  $\sigma(0)$ , when it occurs, is  $(-1)^s(2g+1)$ , we may evidently equate the  $\sigma$ -expression to zero, for all values of  $n$ , if we put  $\sigma(0)$  equal to  $\frac{1}{6}g(g+1)$ , that is, equal to  $\frac{1}{6}n$ .

§ 9. Since the general theorem is merely concerned with the mutual cancellation of a system of numbers, *i. e.* since it merely asserts that a number which occurs any number of times with the positive sign will occur exactly the same number of times with the negative sign (except in the case of certain numbers, when  $n$  is a triangular number), it is evident that we are at liberty to change the signs of all the even numbers throughout (or, indeed, the signs of all the numbers of any particular form).

Changing the signs of the even numbers, and adding together the numbers in each group, we evidently obtain  $\zeta(n)$  from the first group. The sum of the numbers in the middle line of the second group is  $\zeta(n-1)$ , and the sum of the numbers in the upper and lower lines is  $-2\zeta(n-1)$ . Similarly in the third group the sum of the numbers in the middle line is  $\zeta(n-3)$ , the sum of the numbers in the next upper and next lower lines is  $-2\zeta(n-3)$ , and in the highest and lowest lines is  $2\zeta(n-3)$ ; and so on.

Finally, changing the signs of the alternate groups, we obtain the expression

$$\zeta(n) + \zeta(n-1) + \zeta(n-3) + \zeta(n-6) + \zeta(n-10) + \&c.$$

When the signs of the even numbers are changed, the numbers which remain uncanceled in the general theorem are

$$(-1)^{s-1}\{\text{one } 1, \text{ two } (-2)\text{'s, three } 3\text{'s, } \dots, g(\pm g)\text{'s}\}.$$

Adding these numbers we obtain the series

$$(-1)^{s-1}\{1^2 - 2^2 + 3^2 - 4^2 + \dots + (-1)^{s-1}g^2\},$$

the sum of which is  $\frac{1}{2}g(g+1)$ . We may therefore equate the above  $\zeta$ -expression to zero for all values of  $n$ , if we put  $\zeta(0) = -n$ .

§ 10. In thus deriving the two formulæ from a common origin we obtain, so to speak, an arithmetical reason for their general similarity of form, and for the dissimilarity in their coefficients: in fact, we see that the one result arises in the form

$$\begin{aligned} \sigma(n) - (1+2)\sigma(n-1) + (1+2+2)\sigma(n-3) \\ - (1+2+2+2)\sigma(n-6) + \&c. \\ = 0 \text{ or } (-1)^{s-1}\{1^2+2^2+3^2+\dots+g^2\}, \end{aligned}$$

and the other in the form

$$\begin{aligned} \zeta(n) - (1-2)\zeta(n-1) + (1-2+2)\zeta(n-3) \\ - (1-2+2-2)\zeta(n-6) + \&c. \\ = 0 \text{ or } (-1)^{s-1}\{1^2-2^2+3^2-\dots+(-1)^{s-1}g^2\}. \end{aligned}$$

§ 11. Between the  $\sigma$ - and  $\zeta$ -formulæ which involve as arguments all the numbers from unity to  $n$ , the resemblance is even closer.

The  $\sigma$ -formula may be written

$$\begin{aligned} \sigma(n) - 2\sigma(n-1) - 2\sigma(n-2) + 3\sigma(n-3) + 3\sigma(n-4) \\ + 3\sigma(n-5) - 4\sigma(n-6) - 4\sigma(n-7) - \dots + (-1)^{p-1}p\sigma(0) = 0, \end{aligned}$$

where  $\sigma(0)$  is to receive the conventional value  $\frac{1}{6}(p^2-1)$ ,  $p$  being defined as the coefficient of  $\sigma(0)$ .

The corresponding  $\zeta$ -formula is

$$\begin{aligned} \zeta(n) + 2\zeta(n-1) + 2\zeta(n-2) + 3\zeta(n-3) + 3\zeta(n-4) \\ + 3\zeta(n-5) + 4\zeta(n-6) + 4\zeta(n-7) + \dots + p\sigma(0) = 0, \end{aligned}$$

where  $\zeta(0)$  has the value  $-\frac{1}{6}(p^2-1)^*$ .

The two formulæ have the same coefficients, *i. e.* the first term has the coefficient unity, the next two have the coefficient 2, the next three 3, and so on; and they differ only in the signs of the groups with even coefficients, which are negative in the  $\sigma$ -formula. The values assigned to  $\sigma(0)$  and  $\zeta(0)$  are the same in magnitude for the same value of  $n$  or  $p$ , and differ only in sign.

§ 12. As before, we find that both formulæ may be deduced from a general theorem relating to the actual divisors of the numbers  $n$ ,  $n-1$ ,  $n-2$ , &c. by adding the numbers in the groups, and by adding the numbers in the groups after changing the signs of the even numbers.

\* These formulæ were given in *Proc. Lond. Math. Soc.* vol. xv. (1884) pp. 118, 119; and *Proc. Camb. Phil. Soc.* (1884) p. 119.

§ 13. Using the same notation as in § 4 the general theorem may be stated :—

The numbers given by the formula

$$G(d) - (G_{n-1} + G_{n-2})(d \pm 1) + (G_{n-3} + G_{n-4} + G_{n-5})(d, d \pm 2) \\ - (G_{n-6} + \dots + G_{n-9})(d \pm 1, d \pm 3) \\ + (G_{n-10} + \dots + G_{n-14})(d, d \pm 2, d \pm 4) - \&c.$$

all cancel one another with the exception of

one 1, three 3's, five 5's, ...,  $(p-1)$   $p$ 's, if  $p$  be even,  
and  
two  $(-2)$ 's, four  $(-4)$ 's, six  $(-6)$ 's, ...,  $(p-1)\{- (p-1)\}$ 's,  
if  $p$  be uneven,

where  $\frac{1}{2}p(p+1)$  is the triangular number next superior to  $n$ .

§ 14. As an example let  $n=9$ , so that  $\frac{1}{2}p(p+1)=10$ , and therefore  $p=4$ .

We first form the groups of numbers

$$\begin{array}{cccccccc} & & & & 4, 6, & 4, & 5, & 4 \\ & 2, 3, 5, 9, & 2, 8 & 3, 4, 5, 8, & 3, 7, & 3, 4, 6, & 2, 4, & 2, 3, & 2 \\ 1, 3, 9; & (1, 2, 4, 8; & 1, 7); & 1, 2, 3, 6; & 1, 5; & 1, 2, 4; & (1, 3; & 1, & 2; & 1) \\ & 0, 1, 3, 7, & 0, 6 & -1, 0, 1, 4, & -1, 3, & -1, 0, 2, & 0, 2, & 0, & 1, & 0 \\ & & & & & & -2, 0, & -2, & -1, & -2 \end{array}$$

in which the central line contains, in the first group, the divisors of 9, in the second group those of 8, 7, in the third group those of the next three numbers 6, 5, 4, and in the fourth group those of the remaining numbers 3, 2, 1. The numbers derived from them, *i. e.*  $d+1$  and  $d-1$  in the second group,  $d+2$  and  $d-2$  in the third group, and  $d+1$ ,  $d+3$ , and  $d-1$ ,  $d-3$  in the fourth group, are then written above and below. The divisors in the second and fourth groups are enclosed in brackets to indicate that they do not belong to the scheme of numbers, being merely written down for the sake of deducing from them the numbers  $d \pm 1$ , &c. Changing the signs of the numbers in the second and fourth groups, we obtain the system of numbers

$$\begin{array}{cccccccc} & & & & -4, & -6, & -4, & -5, & -4 \\ & & & 3, 4, 5, 8, & 3, 7, & 3, 4, 6, & & & \\ -2, & -3, & -5, & -9, & -2, & -8, & -2, & -4, & -2, & -3, & -2 \\ 1, 3, 9, & & & 1, 2, 3, 6, & 1, 5, & 1, 2, 4, & & & \\ & 0, & -1, & -3, & -7, & 0, & -6, & 0, & -2, & 0, & -1, & 0 \\ & & & & & & & -1, & 0, & 1, & 4, & -1, & 3, & -1, & 0, & 2, \\ & & & & & & & & & & & & & & & 2, & 0, & 2, & 1, & 2 \end{array}$$

all of which, the theorem asserts, cancel each other with the exception of 1, 3, 3, 3.

§ 15. Adding the numbers in each group, we evidently obtain the expression

$$\sigma(n) - 2\{\sigma(n-1) + \sigma(n-2)\} + 3\{\sigma(n-3) + \sigma(n-4) + \sigma(n-5)\} \\ - 4\{\sigma(n-6) + \dots + \sigma(n-9)\} + \&c.;$$

and the sum of the numbers which remain uncanceled is

$$1^2 + 3^2 + 5^2 + \dots + (p-1)^2$$

or

$$-\{2^2 + 4^2 + 6^2 + \dots + (p-1)^2\}$$

according as  $p$  is even or uneven.

Now,  $p$  being even,

$$1^2 + 3^2 + 5^2 + \dots + (p-1)^2 = \frac{1}{8}(p^3 - p),$$

and,  $p$  being uneven,

$$2^2 + 4^2 + 6^2 + \dots + (p-1)^2 = \frac{1}{8}(p^3 - p),$$

so that, for all values of  $p$ , the  $\sigma$ -expression is equal to  $(-1)^{\frac{p}{2}} \frac{1}{8}(p^3 - p)$ . It is easy to see that  $p$ , defined by the fact that  $\frac{1}{2}p(p+1)$  is the triangular number next superior to  $n$ , is the same as the  $p$  of § 11, which was defined as the coefficient of  $+\sigma(0)$  in the formula: we may therefore equate the  $\sigma$ -expression to zero if we put  $\sigma(0) = \frac{1}{8}(p^3 - 1)$ .

§ 16. Similarly by changing the signs of the even numbers and then adding the numbers in each group we find that the expression

$$\zeta(n) + 2\{\zeta(n-1) + \zeta(n-2)\} + 3\{\zeta(n-3) + \zeta(n-4) + \zeta(n-5)\} \\ + 4\{\zeta(n-6) + \dots + \zeta(n-9)\} + \&c.$$

is equal to

$$1^2 + 3^2 + 5^2 + \dots + (p-1)^2 \text{ or } 2^2 + 4^2 + 6^2 + \dots + (p-1)^2$$

according as  $p$  is even or uneven. By replacing these series by their sums, as in the preceding section, we obtain the result in the form given in § 11.

§ 17. The general theorems of §§ 4 and 13 were proved in a paper which was communicated to the London Mathematical Society last May.\* They are there deduced from analytical formulæ connected with the Zeta Functions. A purely arithmetical proof of them would be very interesting, and it is probable that it would be easier to obtain such a proof for the general theorems than for the recurring formulæ which are deducible from them by addition.

There are various other general theorems relating to the actual divisors which reduce to the recurring formulæ of §§ 1, 2, and 11 when the numbers in each group are added

\* "Relations between the Divisors of the first  $n$  natural numbers:" read May 14, 1891.



together. Some of these theorems are given in the paper just referred to, and others in a continuation which will shortly be communicated to the same Society. In this note I have only mentioned the two theorems which give rise to  $\sigma$ -formulæ by simple addition, and to the corresponding  $\zeta$ -formulæ by addition after changing the signs of the even numbers, my object being merely to supply an arithmetical explanation of the general resemblance, and differences in detail, which are observable in corresponding pairs of  $\sigma$ - and  $\zeta$ -formulæ.

§ 18. The recurring formulæ which are deducible from the general theorems by adding the cubes and higher uneven powers of the numbers in each group, and adding the same powers after changing the signs of the even numbers, necessarily exhibit the same kinds of resemblance and discrepancy as the  $\sigma$ - and  $\zeta$ -formulæ of §§ 1, 2, and 11.

§ 19. Thus, for example, by adding the cubes of the numbers in the general theorem of § 4 we find

$$\begin{aligned} \sigma_3(n) - 3\sigma_3(n-1) + 5\sigma_3(n-3) - 7\sigma_3(n-6) + 9\sigma_3(n-10) - \&c. \\ - 6\{\sigma(n-1) - (1^2 + 2^2)\sigma(n-3) + (1^2 + 2^2 + 3^2)\sigma(n-6) - \&c.\} \\ = [(-1)^{g-1}\{1^4 + 2^4 + 3^4 + \dots + g^4\}], \end{aligned}$$

where  $\sigma_3(n)$  denotes the sum of the cubes of all the divisors of  $n$ , and the term enclosed in square brackets only occurs when  $n$  is a triangular number,  $\frac{1}{2}g(g+1)$ . When  $n$  is not a triangular number the right-hand member of the equation is zero.

By adding the cubes of the numbers, after changing the signs of the even numbers, we find

$$\begin{aligned} \zeta_3(n) + \zeta_3(n-1) + \zeta_3(n-3) + \zeta_3(n-6) + \zeta_3(n-10) \\ + 6\{\zeta(n-1) - (1^2 - 2^2)\zeta(n-3) + (1^2 - 2^2 + 3^2)\zeta(n-6) - \&c.\} \\ = [(-1)^{g-1}\{1^4 - 2^4 + 3^4 - \dots + (-1)^{g-1}g^4\}], \end{aligned}$$

where  $\zeta_3(n)$  denotes the excess of the sum of the cubes of the uneven divisors of  $n$  above the sum of the cubes of the even divisors, and the square brackets have the same meaning as in the case of the  $\sigma$ -formula.

Reducing the expressions on the left-hand side of these equations, they become respectively

$$\begin{aligned} \sigma_3(n) - 3\sigma_3(n-1) + 5\sigma_3(n-3) - 7\sigma_3(n-6) + 9\sigma_3(n-10) - \&c. \\ - 2\{3\sigma(n-1) - 5 \cdot 3\sigma(n-3) + 7 \cdot 6\sigma(n-6) - 9 \cdot 10\sigma(n-10) + \&c.\} \\ \text{and} \\ \zeta_3(n) + \zeta_3(n-1) + \zeta_3(n-3) + \zeta_3(n-6) + \zeta_3(n-10) + \&c. \\ + 6\{\zeta(n-1) + 3\zeta(n-3) + 6\zeta(n-6) + 10\zeta(n-10) + \&c.\}. \end{aligned}$$

V. *On the Calculation of the Induction-Coefficients of Coils, and the Construction of Standards of Inductance, and on Absolute Electrodynamometers.* By ANDREW GRAY, M.A., *Professor of Physics in the University College of North Wales\**.

IT is well known that the electrokinetic energy of the currents in two circular conductors can be expressed by a series of zonal harmonics. This series, when used in the ordinary way to find the energy of the currents in two cylindrical coils (and hence also the induction-coefficients of the coils) by expansion of each term of the series and subsequent integration, does not yield expressions which are convenient for practical applications, as the work of calculation is long and tedious. I have found, however, that it is possible very simply to integrate each term without expansion; and the result shows that a pair of coils may be constructed in such a way that the zonal harmonic expression reduces to a very manageable form, and the energy of the currents, and therefore the induction-coefficients and mutual action of the coils, can be very readily obtained.

With regard to the construction of coils it is possible, by using fine wire wound by a screw-cutting lathe in a close single layer on an accurately turned cylindric surface, to make a coil of a large number of turns the dimensions of which can be determined very exactly, and in which the distribution of the wire is perfectly definite. Such a single-layer coil I have long advocated for use in absolute galvanometers. It has sufficient uniformity of field to render the placing of the needle at the exact centre quite unessential, and it can be made sufficiently sensitive, so that it possesses the advantages of the Helmholtz double-coil arrangement, without the uncertainty which exists in the latter as to the distribution of the different turns of wire in the two multiple-layer bobbins, or requiring the correction-terms which these bobbins involve on account of their finite cross section.

By integrating the zonal harmonic expression for two circles with intersecting axes, in order to find the corresponding expression for the mutual energy of two single-layer coils, I have obtained a series, the even terms of which all vanish when one at least of the coils is placed with its centre at the intersection of the axes. The third term vanishes if the smaller of the two coils is so placed, and has its length and

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diameter in the ratio of  $\sqrt{3}$  to 2; and the fifth term also disappears when the larger coil fulfils the same conditions. Further, if both coils are thus proportioned and placed, the even terms, so to speak, doubly vanish, so that any little inaccuracy in the placing of the coils can only very slightly affect the result.

We are thus left with the first, seventh, ninth, eleventh, &c. terms of the series. If one coil has half the radius of the other, the error made by taking only the first term in calculating the inductance &c. of the pair of coils is only about 1 in 26,000; and if the ratio of the radii is as great as  $\frac{2}{3}$ , only 1 in 4500.

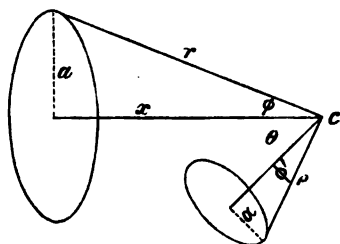
This result is, it seems to me, of importance both as regards the construction of coils to serve as mutual or self-induction standards, and the choice of the proper arrangement of coils for use in an electro-dynamometer for the absolute measurement of currents.

The mutual electrokinetic energy of two circles carrying unit currents is given by the equation

$$T = 4\pi^2 \rho \sin^2 \phi \sin^2 \phi' \sum \frac{1}{i(i+1)} Z_i'(\phi) \cdot Z_i'(\phi') \cdot Z_i(\theta) \left(\frac{\rho}{r}\right)^i; \quad (1)$$

$(\rho < r)$

where, as shown in the figure,  $\phi, \phi'$  are the angles which the



radii of the circles subtend at the intersection,  $c$ , of the axes, which is taken as the origin of the zonal harmonics;  $Z_i'(\phi)$  the differential coefficient with respect to  $\cos \phi$  of the zonal harmonic of the  $i$ th order for the angle  $\phi$ ;  $Z_i'(\phi')$  the corresponding function for  $\phi'$ ;  $Z_i(\theta)$  the zonal harmonic of the  $i$ th order in terms of the angle  $\theta$  between the axes of the circles; and  $r, \rho$ , ( $\rho < r$ ) are the distances of the circular arcs from the origin.

Now instead of two circles take two narrow circular elements of two-single layer coils the axes of which intersect, and the numbers of turns in which per unit of length along the axis are  $n, n'$ . Let  $a$  be the radius of one element, and  $x$  its axial

distance from the origin ;  $a, \xi$  the corresponding quantities for the other, so that  $r = \sqrt{x^2 + a^2}$ ,  $\rho = \sqrt{\xi^2 + a^2}$ ; and let  $dx, d\xi$  be the axial lengths of the elements. Then if unit current flow in each turn of the coils the currents in the elements are  $n dx, n' d\xi$ . Writing down, then, by (1) the expression for the energy of the two elements, and integrating from  $x = x_1$  to  $x = x_2$  in the one case, and from  $\xi = \xi_1$  to  $\xi = \xi_2$  in the other, we get for the mutual electrokinetic energy of two coils of lengths  $x_2 - x_1, \xi_2 - \xi_1$ , and carrying unit currents, the expression

$$T = 4\pi^2 n n' a^2 \sum \frac{1}{i(i+1)} Z_i(\theta) \left\{ \int_{x_1}^{x_2} \frac{Z_i'(\phi)}{r^{i+2}} dx \right\} \left\{ \int_{\xi_1}^{\xi_2} \rho^{i-1} Z_i(\phi') d\xi \right\}. \quad (2)$$

$Z_i'(\phi')$  is found by differentiation with respect to  $\cos \phi'$  from the well-known expression, and  $\xi/\rho$  then written for  $\cos \phi'$  converts the result into a fraction the numerator of which is a rational integral function of  $\xi$  only, and the denominator of which is  $\rho^{i-1}$ . This denominator is cancelled by the multiplier  $\rho^{i-1}$ , and the second integral can thus be found at once in all cases without any difficulty.  $Z_i'(\phi)$  can also be found by differentiation in the same manner, and the integral then found by direct integration for each value of  $i$ ; but the following process, which gives by successive differentiation of a simple function at once the indefinite integrals required for the evaluation of the first definite integral, and the values of  $Z_i'(\phi)$ , is much more convenient.

The solid angle subtended by one of the circles, say that of radius  $a$  and axial distance  $x$ , at a point distant  $\rho$  from the origin is given if  $\rho < r$  by the equation

$$\omega = 2\pi \left\{ 1 - \cos \phi + \sin^2 \phi \sum \frac{1}{i} Z_i'(\phi) Z_i(\theta) \left( \frac{\rho}{r} \right)^i \right\}, \quad (3)$$

where  $\theta$  is the angle between the axis of the circle and the line from the origin to the point in question.

Now let the angle  $\theta$  be  $90^\circ$ , and  $a$  be zero, so that  $\rho$  is the distance,  $y$ , of the point considered from the axis; then all the harmonics  $Z_i(\theta)$  of odd order vanish, and the general expression for the harmonic of even order  $2i$  is

$$(-1)^i \frac{1 \cdot 3 \dots (2i-1)}{2 \cdot 4 \dots 2i}.$$

Hence

$$\omega = 2\pi \left[ 1 - \frac{x}{r} - a^2 \left\{ \frac{1}{2^2} \frac{y^2}{r^4} Z_2'(\phi) - \frac{1 \cdot 3}{2 \cdot 4^2} \frac{y^4}{r^6} Z_4'(\phi) + \dots \right\} \right]. \quad (4)$$

But this is of the form

$$\omega = 2\pi(A_0 + A_1y^2 + A_2y^4 + \dots), \quad \dots \quad (5)$$

where  $2\pi A_0$  is the value of  $\omega$  for  $y=0$ , so that  $A_0=1-x/r$ . Now  $\omega$  must satisfy Laplace's equation, which, since there is symmetry round the axis of the circle, is for the present case,

$$\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} + \frac{1}{y} \frac{\partial \omega}{\partial y} = 0. \quad \dots \quad (6)$$

Differentiating (5) and substituting in (6) we find

$$\begin{aligned} & \frac{\partial^2 A_0}{\partial x^2} + \frac{\partial^2 A_1}{\partial x^2} y^2 + \frac{\partial^2 A_2}{\partial x^2} y^4 + \dots \\ & + 2A_1 + 3 \cdot 4A_2y^2 + 5 \cdot 6A_3y^4 + \dots \\ & + 2A_1 + 4A_2y^2 + 6A_3y^4 + \dots = 0. \end{aligned}$$

The coefficients of the different powers of  $y$  in this series equated separately to zero give

$$A_1 = -\frac{1}{2^2} \frac{\partial^2 A_0}{\partial x^2}, \quad A_2 = \frac{1}{2^2 \cdot 4^2} \frac{\partial^4 A_0}{\partial x^4}, \quad A_3 = -\frac{1}{2^2 \cdot 4^2 \cdot 6^2} \frac{\partial^6 A_0}{\partial x^6}, \dots$$

so that

$$\omega = 2\pi \left( A_0 - \frac{y^2}{2^2} \frac{\partial^2 A_0}{\partial x^2} + \frac{y^4}{2^2 \cdot 4^2} \frac{\partial^4 A_0}{\partial x^4} - \dots \right). \quad \dots \quad (7)$$

Comparing this with (4) we have

$$a^2 \frac{Z_2'(\phi)}{r^4} = \frac{\partial^2 A_0}{\partial x^2},$$

$$3! a^2 \frac{Z_4'(\phi)}{r^6} = \frac{\partial^4 A_0}{\partial x^4},$$

$$5! a^2 \frac{Z_6'(\phi)}{r^8} = \frac{\partial^6 A_0}{\partial x^6}.$$

.....

Thus we have, neglecting constants,

$$\left. \begin{aligned} a^2 \int \frac{Z_2'(\phi)}{r^4} dx &= \frac{\partial A_0}{\partial x} \\ 3! a^2 \int \frac{Z_4'(\phi)}{r^6} dx &= \frac{\partial^3 A_0}{\partial x^3} \end{aligned} \right\} \dots \quad (8)$$

.....

and we are able to calculate the integrals of even order required for (2) by successive differentiation of  $A_0 (= 1 - x/r)$ .

To find the integrals of odd order let us assume that

$$A \int \frac{Z'_{2i+1}(\phi)}{r^{2i+3}} dx = \frac{\partial^{2i} A_0}{\partial x^{2i}}, \dots \dots \dots (9)$$

where  $A$  is a constant. Differentiating, we obtain from this equation and (8) the relation

$$A \frac{Z'_{2i+1}(\phi)}{r^{2i+3}} = \frac{\partial^{2i+1} A_0}{\partial x^{2i+1}} = (2i+1)! a^2 \int \frac{Z'_{2i+2}(\phi)}{r^{2i+4}} dx,$$

and therefore also

$$\begin{aligned} A \{ (1 - \mu^2) Z''_{2i+1}(\phi) - (2i+3) \mu Z'_{2i+1}(\phi) \} \\ = (2i+1)! a^2 Z'_{2i+2}(\phi), \dots \dots \dots (10) \end{aligned}$$

where  $\mu = \cos \phi$ .

The assumption made in (9) will be justified if the relation expressed in (10) holds for a constant value of  $A$ . Now if  $Z_i$  denote a zonal harmonic of any order  $i$ , we have by the fundamental relations of zonal harmonics

$$\mu Z_i - Z_{i-1} = -\frac{1}{i} (1 - \mu^2) Z'_i,$$

$$Z_i - \mu Z_{i-1} = -\frac{1}{i} (1 - \mu^2) Z'_{i-1}.$$

From these equations we find by elimination of  $Z_{i-1}$ ,

$$Z_i = \frac{1}{i} (\mu Z'_i - Z'_{i-1}); \dots \dots \dots (11)$$

and by elimination of  $Z_i$ ,

$$Z_{i-1} = \frac{1}{i} (Z'_i - \mu Z'_{i-1}). \dots \dots \dots (11')$$

Differentiating (11) and (11') with respect to  $\mu$  and eliminating  $Z'_i$ , we get the relation

$$(1 - \mu^2) Z''_{i-1} - \mu(i+1) Z'_{i-1} = -(i-1) Z'_i;$$

which, with  $2i+2$  written for  $i$ , agrees with (10) if we put

$$A = -(2i-1)! a^2.$$

This verifies the assumption.

Thus we have, neglecting constants as before,

$$\left. \begin{aligned} a^2 \int \frac{Z_1'(\phi)}{r^3} dx &= -A_0, \\ 2! a^2 \int \frac{Z_2'(\phi)}{r^5} dx &= -\frac{\partial^2 A_0}{\partial x^2}, \\ 4! a^2 \int \frac{Z_3'(\phi)}{r^7} dx &= -\frac{\partial^4 A_0}{\partial x^4}, \\ &\dots \dots \dots \end{aligned} \right\} \dots \dots (8')$$

Thus (8) and (8') give by the same process all the required integrals. Taken together they give the theorem

$$\int \frac{Z_i'(\phi)}{r^{i+2}} dx = (-1)^i \frac{1}{i! a^2} \frac{\partial^{i-1} A_0}{\partial x^{i-1}}, \quad \dots \dots (12)$$

where  $i$  is any positive integer. A similar theorem holds of course, *mutatis mutandis* (that is, with  $a$  substituted for  $\alpha$ ,  $\xi$  for  $x$ , and  $\rho$  for  $r$ ), for the harmonics in  $\phi'$ , and can be used as indicated above for the calculation of the second integrals in (2).

The first seven derived functions of  $A_0$  are as follows:—

$$\begin{aligned} A_0 &= 1 - \frac{x}{r}, \\ \frac{\partial A_0}{\partial x} &= -\frac{a^2}{r^3}, \\ \frac{\partial^2 A_0}{\partial x^2} &= \frac{3a^2 x}{r^5}, \\ \frac{\partial^3 A_0}{\partial x^3} &= -3 \frac{a^2}{r^7} (4x^2 - a^2), \\ \frac{\partial^4 A_0}{\partial x^4} &= 3 \cdot 5 \frac{a^2 x}{r^9} (4x^2 - 3a^2), \\ \frac{\partial^5 A_0}{\partial x^5} &= -3^2 \cdot 5 \frac{a^3}{r^{11}} (8x^4 - 12x^2 a^2 + a^4), \\ \frac{\partial^6 A_0}{\partial x^6} &= 3^3 \cdot 5 \frac{a^3 x}{r^{13}} (56x^4 - 140x^2 a^2 + 35a^4), \\ \frac{\partial^7 A_0}{\partial x^7} &= -3^3 \cdot 5 \frac{a^3}{r^{15}} (448x^6 - 1680x^4 a^2 + 840x^2 a^4 - 35a^6). \end{aligned}$$

Substituting these values in (8), (8'), or (12), and using the results in (2), we obtain

$$T = \pi^2 n n' a^2 \alpha^2 \{ K_1 k_1 Z_1(\theta) + K_2 k_2 Z_2(\theta) + \dots \}, \quad \dots (13)$$

where

$$K_1 = \frac{2}{a^2} \left( \frac{x_2}{r_2} - \frac{x_1}{r_1} \right), \quad K_2 = - \left( \frac{1}{r_2^3} - \frac{1}{r_1^3} \right),$$

$$K_3 = - \frac{1}{2} \left( \frac{x_2}{r_2^5} - \frac{x_1}{r_1^5} \right), \quad K_4 = - \frac{1}{8} \left\{ \frac{1}{r_2^7} (4x_2^2 - a^2) - \frac{1}{r_1^7} (4x_1^2 - a^2) \right\},$$

$$K_5 = - \frac{1}{8} \left\{ \frac{x_2}{r_2^9} (4x_2^2 - 3a^2) - \frac{x_1}{r_1^9} (4x_1^2 - 3a^2) \right\},$$

$$K_6 = - \frac{1}{8} \left\{ \frac{1}{r_2^{11}} \left( 4x_2^4 - 6x_2^2 a^2 + \frac{1}{2} a^4 \right) - \frac{1}{r_1^{11}} \left( 4x_1^4 - 6x_1^2 a^2 + \frac{1}{2} a^4 \right) \right\},$$

$$K_7 = - \frac{1}{8} \left\{ \frac{x_2}{r_2^{13}} \left( 4x_2^4 - 10x_2^2 a^2 + \frac{5}{2} a^4 \right) - \frac{x_1}{r_1^{13}} \left( 4x_1^4 - 10x_1^2 a^2 + \frac{5}{2} a^4 \right) \right\},$$

$$\dots \dots \dots$$

$$k_1 = \xi_2 - \xi_1, \quad k_2 = \xi_2^2 - \xi_1^2,$$

$$k_3 = 2\xi_2^3 - \frac{3}{2} \xi_2 \alpha^2 - 2\xi_1^3 + \frac{3}{2} \xi_1 \alpha^2, \quad k_4 = 2\xi_2^4 - 3\xi_2^2 \alpha^2 - 2\xi_1^4 + 3\xi_1^2 \alpha^2,$$

$$k_5 = 2\xi_2^5 - 5\xi_2^3 \alpha^2 + \frac{5}{4} \xi_2 \alpha^4 - 2\xi_1^5 + 5\xi_1^3 \alpha^2 - \frac{5}{4} \xi_1 \alpha^4,$$

$$k_6 = 2\xi_2^6 - \frac{15}{2} \xi_2^4 \alpha^2 + \frac{15}{4} \xi_2^2 \alpha^4 - 2\xi_1^6 + \frac{15}{2} \xi_1^4 \alpha^2 - \frac{15}{4} \xi_1^2 \alpha^4,$$

$$k_7 = 2\xi_2^7 - \frac{21}{2} \xi_2^5 \alpha^2 + \frac{35}{4} \xi_2^3 \alpha^4 - \frac{35}{32} \xi_2 \alpha^6 - 2\xi_1^7 + \frac{21}{2} \xi_1^5 \alpha^2 - \frac{35}{4} \xi_1^3 \alpha^4 + \frac{35}{32} \xi_1 \alpha^6.$$

If one of the coils, say that of radius  $a$ , have its centre at the origin,  $x_2 = -x_1$ , and the terms of even order all vanish since  $k_2, k_4, \&c.$  vanish. If, besides, the other coil have its centre at the origin,  $\xi_2 = -\xi_1$ , and the even terms doubly vanish.

Further, if besides being so placed the second coil be constructed so that its length  $2\xi_2 = \sqrt{3}a$ , the third term of the series in (13) will vanish; and similarly the fifth term will disappear if the first coil fulfil the relation  $2x_2 = \sqrt{3}a$ . Thus, under the conditions specified, all the terms in (13) between the first and seventh disappear.

The first term will give T to a sufficient degree of approximation for all practical purposes if  $\alpha \gg 2a/3$ , as then the coefficient of  $Z_7(\theta)$  does not amount to more than  $1/4500$  of that of  $Z_1(\theta)$ , and the terms of higher order are relatively unimportant. If  $\alpha \gg a/2$  the seventh coefficient in (13) is, at most, only about  $1/26,000$  of that of the first.



Since the currents in the coils are each unity, the expression in (13) is the coefficient of mutual induction  $M$  of the two coils. By constructing the coils in the manner here specified, and placing them so as to be concentric and coaxial,  $Z_1(\theta) = 1$ , and the coefficient of mutual induction is, if  $a \gg 2a/3$ , practically given by the equation

$$M = 8\pi^2 mn' a^2 \frac{x_2 \xi_2}{r_2}, \quad . \quad . \quad . \quad . \quad (14)$$

where  $x_2, \xi_2$  are the half-lengths of the coils.

Accurate standards of mutual inductance could thus, I venture to think, be very conveniently constructed.

Equation (13) gives of course also the coefficient of self-induction of a coil. It is only necessary to make the coils equal in size and coincident and take the value of  $T$  so given as the required coefficient. The first term will not in this case suffice for so high a degree of approximation, although the series is still fairly convergent.

The application of these results to the construction of absolute electro-dynamometers is also obvious. By making one coil small enough to be suspended concentrically within the other, but not so small as to render the exact measurement of its dimensions difficult, we can construct an instrument the constant of which is easily calculated with great accuracy. The couple  $\Theta$  turning the suspended coil would then for unit current in each be given by

$$\Theta = -8\pi^2 nn' a^2 \frac{x_2 \xi_2}{r_2} \sin \theta. \quad . \quad . \quad . \quad . \quad (15)$$

Should, instead of single-layer coils, coils of several layers be employed, the channels in which the wire is wound might be so shaped as to cause each layer to fulfil as nearly as possible the ratio of length to diameter stated above. This might be done by making the ends of each channel segments of a cone the vertex of which is at the centre of the coil, and the semi-vertical angle of which is  $\tan^{-1} \sqrt{3}/2$ . Then, by calculating for all the different pairs of layers which can be obtained by taking one layer in each coil, the energy of the arrangement and the action of one coil on the other might be found. The accuracy of such an arrangement would of course be limited by the fact that if one layer (as would always be arranged) fulfilled the required relation of length to diameter with an exact number of turns, the rest might only more or less closely approximate to such fulfilment. There would also be uncertainty as to the distribution of the wire, which would be more or less irregular.

VI. *The Influence of Flaws and Air-cavities on the Strength of Materials.* By J. LARMOR, M.A., Fellow of St. John's College, Cambridge\*.

IN practical estimates of the strength of materials it is usual to take the greatest compressive or tensile stress which the material is found in experiment to sustain, and divide it by a factor of safety to insure against sudden applications and reversals of the load, and against flaws or sources of weakness that cannot be foreseen. Among the latter, cavities or air-bubbles in the material hold a place; and these may also be taken in a general way for purposes of calculation as the type of flaws consisting of a defect or weakening which is confined to a limited volume of the substance.

Thus, in the case of a shaft transmitting a torque or couple, the shearing-stress is annulled over the volume of the cavity, and this may lead to greater than average shearing-stress in some part of its immediate neighbourhood. In the case of a column supporting a load, the supporting thrust is absent over the part of the cross section occupied by the cavity, and this defect of support must be compensated by a greater thrust elsewhere.

When the cavity or flaw is at a great distance from the surface of the casting compared with its linear dimensions, the changes produced by it in the intensity of the stress are the same at corresponding points, whatever be the dimensions of the cavity. For when the latter is altered in linear dimensions but not in form, and the displacement of the material at corresponding points is altered in the same ratio, the components of the strain will maintain their intensities unaltered at corresponding points, and so will the components of the stress. Thus the traction over the surface of the cavity will be unaltered, and therefore remain zero; while the displacements over the surface will be changed in the above ratio. The practical statement of this principle of similarity is that the effect which is produced by a cavity on the strength of a piece under uniform stress is dependent on the form but not on the size of the cavity, provided the distance of the nearest part of the surface from it is at least two or three times its greatest diameter.

The amount of this increase of internal stress determines the theoretical factor of safety which the possibility of a flaw of the type in question would necessitate; and it is possible to arrive at an estimate for the case of spherical or cylindrical

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cavities, which may be of use as a general indication of the order of magnitude involved in other similar cases also. Even for the actual cases worked out the result is not, however, to be interpreted exactly. For, in the first place, to make calculation possible the proportionality of stress to strain (Hooke's law) is assumed, and this ceases to hold, the material sometimes even begins to flow, before the critical condition is attained; and, secondly, the conditions that produce a breakdown of the material are but vaguely understood.

A spherical portion of the mass becomes, when strained, an ellipsoid of which the principal axes determine the three principal elongations which constitute the strain. Now it is sometimes assumed that a simple change of volume by compression or expansion cannot produce or affect rupture, and therefore this ellipsoid need only be compared with the sphere of equal volume from which it is derived by three simple shears in mutually rectangular planes. The value of the greatest of these shears may then perhaps be taken to be the circumstance determining the limiting strength of the material. It may, however, be remarked that, as the forces of cohesion between the elements of the material are not infinite, it must be possible to break it down or pull it asunder by a tension uniform in all directions (say a negative hydrostatic pressure); and it is quite conceivable that a pressure equal in all directions may by the opposite displacement loosen the bonds of cohesion and so produce a plastic condition which will give other forces play to act. The experiments of W. Spring, in which an intimate mixture of two solid substances which do not combine chemically under ordinary circumstances is caused to combine by the application of great pressure, may have a bearing on this question. The fact that cast iron supports compression much better than tension is also in point. If it is, however, the case with any material that the range of tension uniform in all directions which it can stand is very much greater than the range of stresses involving shear, the rupture would depend for that material on the shears only, and the greatest of them might be taken to be its determining cause. Thus rupture would be determined by the difference between the greatest and least axes of the ellipsoid into which a sphere of unit radius is strained. When this supposition is not valid the greatest elongation would be a more likely criterion; but in any case the assumed law will be a sufficient indication for our purpose, because any more precise specification would be vitiated in its application by the causes above mentioned, which render elastic calculations illustrative rather than exact

when pushed towards the limit of strength of the materials. In the most important examples we shall be concerned only with shears.

It will appear on consideration that a small spherical cavity in a column or other mass under tension or compression cannot seriously affect its strength. For its strength could be reduced only by an increase of shear in the neighbourhood of the cavity. Now this shear must act all round it in the planes containing that diameter which lies along the direction of the stress, and at the free surface of the cavity it must be zero, in the absence of surface-tractions there; hence the shear is diminished in the neighbourhood of the cavity. The compression may be slightly increased in a ratio depending on that of the area of the section of the cavity to the area of the section of the shaft. The same argument applies of course to any symmetrical form of cavity, and generally to any cavity of regular shape.

The case is different, however, when the cavity exists in a shaft which transmits a couple. If we suppose the cavity to consist of a narrow tunnel bored down the length of the shaft, we may make use of the result of St. Venant's torsion problem. The distribution of the shear across the section of the shaft is simply and succinctly expressed by hydrodynamical analogy\*. If a cylindrical shell of the same form of cross section as the shaft is filled with frictionless fluid and is set in rotation, the velocity of the fluid relative to the shell will at each point represent the shear, in direction and magnitude; and the momentum of the fluid relative to the shell, which must necessarily have no linear component, will be proportional to the torsional rigidity of the shaft. For the present purpose it is convenient to state the proposition in a form less practically realizable: suppose the shell fixed and the fluid circulating inside it with uniform vorticity, the velocity at each point will represent the shear, and its resultant momentum (angular) will be proportional to the rigidity of the shaft.

Now the result of boring a small tunnel will be to modify the velocity system in the neighbourhood in the same way as a solid cylinder changes the velocities in a stream flowing past it. The velocities in front and rear are reduced to zero, while those at the sides are doubled. A tunnel of this kind therefore halves the strength of the portion of the shaft in which it is situated; and the same statement practically applies to any cavity of elongated form and circular section which lies parallel to the axis of the shaft. The possibility of

\* Thomson and Tait's 'Natural Philosophy,' § 705.

a flaw of this kind near the part of the cross section where the shear is greatest will therefore necessitate the use of a factor of safety equal to two. As the cavity is taken shorter in proportion to its diameter, its effect might at first sight be taken to diminish till we come to the spherical form, which is again amenable to calculation, though with considerable intricacy: we might perhaps expect for it a factor considerably less than two. The result of the mathematical investigation for a spherical cavity which follows, for which I am indebted to Mr. A. E. H. Love, gives, however, a factor which is never very far from the value two, unless the material is but slightly compressible, like a jelly. If we now suppose the spherical cavity to elongate in a direction perpendicular to the shear the factor may be expected still to diminish; and when it is so long as to be sensibly cylindrical the shear is itself diminished in its neighbourhood, for reasons specified above. But if it elongates in the direction perpendicular to the axis of the shaft, and in the plane of the shear, the factor two is recovered.

If the cylindrical cavity is of flat cross section the hydrodynamical analogy shows that its action is intensified. If it were absolutely flat with a sharp edge the strain would be infinite there and rupture would take place, unless in the test there is a chance of smoothing the edge of the flaw by a local flow or adjustment of the material.

A semicircular groove, running along the surface of a shaft, would (in the absence of local flow) nearly halve its torsional strength.

#### *Adaptation of St. Venant's Solution for a Shaft.*

The displacement in St. Venant's solution is

$$u = \omega yz, \quad v = -\omega xz, \quad w = f(x, y);$$

where  $u, v$  represent a simple torsion round the axis of  $z$ , and  $w$  represents the warping of the cross section which is necessary to annul the shear in a plane normal to the free boundary.

The value of this shear is  $\frac{dw}{dn} - \omega p$ , where  $p$  is the perpendicular from the axis on the tangent plane to the boundary, and  $dn$  is an element of the normal. Thus the boundary condition is

$$\frac{dw}{dn} = \omega p;$$

and these displacements maintain internal equilibrium provided

$$\nabla^2 w = 0.$$

These equations show that  $w$  is the velocity-potential of the absolute motion in space of liquid contained in a box rotating with angular velocity  $\omega$ .

The tractions exerted across the section of the shaft are (with unit rigidity)

$$X = \omega y + \frac{dw}{dy}, \quad Y = -\omega x + \frac{dw}{dx}.$$

These must vanish when integrated over the area of the section; therefore the box containing liquid must be supposed to rotate round an axis through the centre of gravity of the section.

The couple transmitted across the section is

$$\begin{aligned} G &= -\int (Xy - Yx) dS \\ &= \int \omega(x^2 + y^2) dS - \int \left( y \frac{dw}{dx} - x \frac{dw}{dy} \right) dS; \end{aligned}$$

it is therefore less than the couple due to simple torsion by the absolute angular momentum of the liquid.

Also  $X, Y$  are the component velocities of liquid circulating in a fixed box with vorticity  $\omega$ ; its resultant velocity represents the shear at each point, and its angular momentum represents the couple transmitted. Its linear momentum is null.

The analysis of this well-known result has been here indicated in full, partly in order to point out that in the first form of the analogy in which the box is made to rotate, the velocity of the liquid relative to the box represents the shear whatever be the axis of rotation, but the angular momentum of the liquid represents the correction to the rigidity only when taken about that axis for which its value is least, viz. the axis through the centre of gravity of the section. If the motion is referred to any other axis, as in the case of a rectangle bounded by two concentric arcs and two radii (Thomson and Tait, § 707), then from the angular momentum round that axis must be subtracted the moment of the linear momentum of the whole mass of fluid supposed collected at its centre of gravity.

Suppose, now, a cylindrical tunnel of small circular section bored down the shaft at a place where the velocity of the rotational fluid motion is  $V$ ; the stream function near it will be changed from the form  $\psi_1 = Vy$  to the form  $\psi_2 = Vy - V \frac{a^2}{r^2} y$ ,

because the boundary of the tunnel,  $r=a$ , must become a stream line, and therefore give a constant value to  $\psi_2$ . The velocity along the tunnel is  $-\frac{d\psi_2}{dn}$ , and is therefore  $2V$  at the sides, as stated above.

The angular momentum of the fluid is altered, owing to the tunnel, by

$$\int \int \frac{d(\psi_2 - \psi_1)}{dy} dx dy,$$

that is  $\int (\psi_2 - \psi_1) \frac{dx}{ds} ds$  round the boundary. For a circular boundary this is equal to  $Va \int \cos^2 \theta ds$ , or  $\pi a^2 V$ . The rigidity of the surrounding parts is therefore diminished by the presence of the cavity, just as if the shearing over the material which originally occupied its place were reversed in direction; the loss of rigidity is due in equal proportion to the removal of the matter and the release on the constraint of the surrounding parts.

The case when the section of the cavity is an elliptic cylinder is of interest, as it illustrates the effect of making it more and more flat until it is finally a mere crack for which the strain is theoretically infinite at the edge. The corresponding hydrodynamical problem has been solved by Prof. Lamb\*: his value of the stream function  $\psi$ , which may easily be verified, is

$$\psi = -V \left( \frac{a+b}{a-b} \right)^{\frac{1}{2}} e^{-\eta} \sin \xi - Vx;$$

where  $a, b$  are the semi-axes of the ellipse,  $V$  is the velocity of the stream past it parallel to the axis  $b$ , and  $\xi, \eta$  are the conjugate functions given by

$$x + iy = c \sin (\xi + i\eta).$$

The velocity at the end of the longer axis is the value of  $d\psi/dx$  when  $y=0$ , that is, when  $\xi = \frac{1}{2}\pi$ , and is found to be

$$V \left( 1 + \frac{a}{b} \right).$$

Thus in the elastic problem the increase of shear produced by the cavity is the original shear multiplied by  $a/b$ .

\* Quart. Journ. of Math. 1875; "Fluid Motion," p. 90.

*Analysis for Spherical Cavity.* (By Mr. Love.)

To investigate the strain in an infinite solid containing a spherical cavity, the displacements at an infinite distance being

$$u=ay, \quad v=0, \quad w=0.$$

From the spherical harmonic solutions of Thomson and Tait it can be shown that the forms of the displacements at a point  $(x, y, z)$  at a distance  $r$  from the centre of the cavity are

$$\left. \begin{aligned} u &= A \frac{y}{r^3} + (B + Cr^2) \frac{d}{dx} \left( \frac{xy}{r^5} \right) + ay, \\ v &= A \frac{x}{r^3} + (B + Cr^2) \frac{d}{dy} \left( \frac{xy}{r^5} \right), \\ w &= (B + Cr^2) \frac{d}{dz} \left( \frac{xy}{r^5} \right), \end{aligned} \right\} \quad \dots \quad (1)$$

where  $A, B, C$  are constants to be determined.

The cubical dilatation  $\delta$  is

$$\delta = -6(A + C) \frac{xy}{r^5} \dots \dots \dots (2)$$

The equations of equilibrium are three such as

$$(\lambda + \mu) \frac{d\delta}{dx} + \mu \nabla^2 u = 0 \quad \dots \dots \dots (3)$$

which gives

$$-(\lambda + \mu)6(A + C) - 10\mu C = 0$$

or

$$3(\lambda + \mu)A + (3\lambda + 8\mu)C = 0. \quad \dots \dots \dots (4)$$

The remaining equations to determine the constants are to be found from the condition that the surface  $r=a$  of the cavity is free from stress. It is shown in Thomson and Tait's Nat. Phil., Part ii., art. 737, that if  $F, G, H$  be the component surface-tractions parallel to the axes across a spherical surface whose centre is the origin and radius is  $r$ , then

$$Fr = \lambda x \delta + \mu \left( \frac{d\xi}{dx} + r \frac{du}{dr} - u \right),$$

where  $\xi = ux + vy + wz$ , and similar equations hold for  $G$  and  $H$ .



Now

$$x\delta = -6(A+C) \frac{x^2y}{r^3},$$

$$\xi = (2A-3C) \frac{xy}{r^3} - 3B \frac{xy}{r^5} + \alpha xy,$$

$$\frac{d\xi}{dx} = (2A-3C) \frac{y}{r^3} - 3B \frac{y}{r^5} - (6A-9C) \frac{x^2y}{r^5} + 15B \frac{x^2y}{r^7} + \alpha y,$$

$$r \frac{du}{dr} - u = -3(A+C) \frac{y}{r^3} - 5B \frac{y}{r^5} + 15C \frac{x^2y}{r^5} + 25B \frac{x^2y}{r^7}.$$

Hence the equations

$$-\left(A + 6C + \frac{8B}{r^3}\right) \frac{y}{r^3} + \alpha y - \left[\frac{\lambda}{\mu} 6(A+C) + 6A - 24C - \frac{40B}{r^3}\right] \frac{x^2y}{r^5} = 0,$$

$$-\left(A + 6C + \frac{8B}{r^3}\right) \frac{x}{r^3} + \alpha x - \left[\frac{\lambda}{\mu} 6(A+C) + 6A - 24C - \frac{40B}{r^3}\right] \frac{xy^2}{r^5} = 0;$$

and similarly from the  $z$  equation

$$-\left[\frac{\lambda}{\mu} 6(A+C) + 6A - 24C - \frac{40B}{r^3}\right] \frac{xyz}{r^5} = 0.$$

These three equations hold when  $r=a$ .

Hence

$$\frac{40B}{a^2} - 6(A+C) \frac{\lambda+\mu}{\mu} + 30C = 0,$$

and

$$\frac{8B}{a^3} + (A+6C) = \alpha a^3.$$

From which and (4) we find

$$\left. \begin{aligned} A &= \frac{3\lambda + 8\mu}{9\lambda + 14\mu} \alpha a^3, \\ B &= \frac{3(\lambda + \mu)}{9\lambda + 14\mu} \alpha a^5, \\ C &= -\frac{3(\lambda + \mu)}{9\lambda + 14\mu} \alpha a^3. \end{aligned} \right\} \dots \dots (5)$$

The shear  $\frac{du}{dy} + \frac{dv}{dx}$  is given by

$$\frac{du}{dy} + \frac{dv}{dx} = \alpha + \frac{2}{r^3} \left( A + C + \frac{B}{r^2} \right) - \frac{x^2 + y^2}{r^5} \left( 8C + 3A + \frac{10B}{r} \right) + \frac{x^2 y^2}{r^7} \left( 50C + \frac{70B}{r^2} \right).$$

To see the magnitude of this take  $x=0, y=0, r=a$ , then

$$\begin{aligned} \frac{du}{dy} + \frac{dv}{dx} &= \alpha \left[ 1 + \frac{10\mu + 6(\lambda + \mu)}{9\lambda + 14\mu} \right] \\ &= \alpha \frac{15\lambda + 30\mu}{9\lambda + 14\mu}, \end{aligned}$$

which depends on the value of  $\lambda/\mu$ , but for all known isotropic materials differs little from  $2\alpha$ .

When  $\lambda/\mu = \infty$ , or the material is incompressible, the shear is

$$\frac{5}{3}\alpha.$$

When  $\mu/\lambda = \infty$ , or the stretch-squeeze ratio vanishes, the shear is

$$\frac{15}{7}\alpha.$$

When  $\lambda = \mu$  (Poisson's condition) the shear is

$$\frac{45}{23}\alpha.$$

St. John's Coll., Cambridge,  
Oct. 26, 1891.

VII. *A Galvanometric Method of Measuring H.* By R. A. LEHFELDT, B.A., B.Sc., Demonstrator at Firth College, Sheffield\*.

IN the ordinary magnetometric, and in Kohlrausch's method of determining the earth's horizontal magnetic force, the magnetic moment or the strength of current is involved, and two observations are necessary to give two equations between which the unknown may be eliminated. If, however, it is assumed that a current can be measured absolutely, the problem of measuring  $H$  is simplified. This may fairly be assumed now, for not only are there very reliable direct-reading ammeters to be had, but the E.M.F. of the Clark cell

\* Communicated by the Author.

and the absolute value of resistances are now known with as great a degree of accuracy as any electrical constants; so that any laboratory possessing a resistance-box and a Clark cell has the means of measuring a current with sufficient accuracy even to replace the Kew magnetometer.

Starting with these considerations, I was led to conclude that the most practical way of measuring the magnetic force would be by running a measured current through an ordinary sensitive reflecting-galvanometer, used either by the tangent, or, preferably, the sine method. For this purpose, a galvanometer and its lamp and scale were fixed on a board and the whole mounted on a goniometer, by which they could be set in any required azimuth; the instrument was first set with its needle parallel to the plane of the coils; a known current passed through it; the goniometer-table rotated till the needle became again parallel to the coils.

Let  $G$  = the principal galvanometer-constant.

$H$  = intensity of the earth's field.

$\gamma$  = current.

$\delta$  = angle of deflexion from the magnetic meridian.

$$G\gamma = H \sin \delta. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The first adjustment necessary is to set the needle parallel to the plane of the coils: this can be done, sufficiently nearly, by making the reflexion of the light from the mirror to coincide with that from the brass face of the instrument. If this is done, it ensures that the galvanometer shall always be used in the same position; and though the needle may make a small angle  $\psi$  with the mean plane, this will only alter the galvanometer-constant in the ratio of  $\cos \psi$ ; so that if we find  $G$  by comparison with a larger measured coil, by Bosscha's method, using the galvanometer in the same position, we shall not make any error.

Next, the suspending fibre may have some torsion. Let  $\phi$  = angle of torsion,

$$\tau = \frac{\text{moment for unit angle of torsion}}{\text{magnetic moment of needle}}$$

Suppose the effect of this torsion is to make the needle lie at an angle  $\theta$  (of the same sign as  $\phi$ ) from the magnetic meridian; then after the goniometer has been rotated through  $\delta$  the needle will make with the meridian the angle  $\delta + \theta$ , and the first equation becomes

$$\gamma G + \tau \phi - H \sin (\delta + \theta) = 0. \quad . \quad . \quad . \quad . \quad (2)$$

If now we take two observations with the galvanometer in positions at right angles to each other and on opposite sides

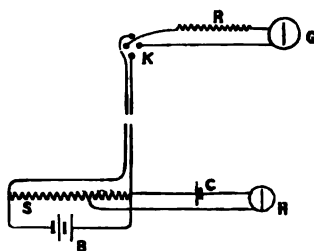
of the meridian, representing these by the suffixes 1 and 2, we have

$$\begin{aligned}\gamma_1 G + \tau\phi - H \sin(\delta_1 + \theta) &= 0, \\ -\gamma_2 G + \tau\phi + H \sin(\delta_2 - \theta) &= 0,\end{aligned}$$

whence

$$H^2 = G^2(\gamma_1^2 + \gamma_2^2) + 2\tau^2\phi^2 + 2\tau\phi G(\gamma_1 - \gamma_2) \quad . \quad (3)$$

By taking  $\delta_1 = \delta_2$ , we shall get  $\gamma_1$  nearly equal to  $\gamma_2$ , and the last term will become almost negligibly small; the middle term is always so. But it is better to use such a pair of observations merely as a preliminary test, to indicate the direction of the torsion, so that it may be removed. I found that, using silk fibres, after turning the torsion-head, the results obtained were at first very irregular; but after successive attempts had reduced the angle of torsion to a small amount, and the fibre had been in use for some days, the elastic after-effects disappeared. So that in a magnetic observatory, where the instrument was always kept for the same purpose, a silk fibre could be used, and once well freed from torsion would probably work quite satisfactorily. The only precautions necessary to note are that, when the needle is deflected by a current, the galvanometer should, without delay, be turned to bring the spot of light back to zero; and that the needle-chamber should be small, not only because



it is convenient to work with well-damped vibrations, but in order that no accidental shaking or current should turn the needle round  $360^\circ$ .

The apparatus was arranged as shown in the diagram :—

B, battery of two storage cells.

C, Clark cell.

G, the principal galvanometer.

H, auxiliary galvanometer for determining the E.M.F.

K, four-part plug-key.

R, adjustable resistance.

S, potentiometer wire-bridge.

The lower portion of the figure represents the potentiometer ; it would, of course, be preferable if this could be replaced by a battery of sufficiently constant E.M.F. capable of giving a milliampere without polarizing. Not knowing of any such battery I was compelled to use accumulators, which will give quite large currents, and vary less than  $\frac{1}{10000}$  part in half an hour, and measure the E.M.F. at each observation.

G was generally a tripod galvanometer of about three ohms' resistance ; with the voltage used, R had to be made about 4000 to give a deflexion of  $45^\circ$ , so that the current used never much exceeded a milliampere ; this was quite insufficient to change the temperature of the coils appreciably. The resistance of G and the leads to it being a very small fraction of R, their temperature-variation was of no account, and only that of R in resistance and C in E.M.F. had to be considered.

The usual procedure was to set the galvanometer G so as to bring the spot of light to zero ; then turn it  $45^\circ$  one way, and apply a current, adjusted by the box R, sufficient to bring the light back to the zero ; then take the potentiometer reading and temperature ; break current ; set the galvanometer at  $45^\circ$  in the other direction from the meridian ; apply the necessary current, the key K being reversed : while this flowed, read the potentiometer again, then break the current, and turn G into its original azimuth, noting that the light returned to the exact position. The whole operation takes scarcely five minutes. Sometimes a longer series of observations was taken, with deflexions of  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ ,  $75^\circ$ , on each side of the meridian, and  $90^\circ$  on one side. The needle is never stable at  $90^\circ$  on both sides at once, as stability there depends on the direction of the torsion. Pairs of observations at  $90^\circ$  apart were taken, and equation (3) applied to calculate H and  $\tau\phi$ . The following is a specimen of the results obtained :—

Deflexions.			H	}	mean 8155
			(in arbitrary units).		
+75°	and	−15°	8178		
+60	„	−30	8154		
+45	„	−45	8155		
+30	„	−60	8156		
+15	„	−75	8156		

The first result is untrustworthy, because for  $\delta = -15^\circ$  R was beyond the range of the resistance-box and had to be found by extrapolation ; the others agree well.

I made no attempt to reduce the results to absolute measure, *Phil. Mag.* S. 5. Vol. 33. No. 200. Jan. 1892. G

because I had no magnetometer at my disposal for comparison, and because the experiments had to be carried on in a building containing a dynamo and other masses of iron. There seems no reason to doubt, however, that with a galvanometer whose constant had been carefully determined, the method would give reliable results.

VIII. *On the Theory of Electrolytic Conduction of Clausius ; and on some recent Evidence for the Dissociation Theory of Electrolysis. By J. BROWN\*.*

THE original theory of Clausius regarding the mechanism of electrolytic conduction is contained in a paper entitled "Ueber die Electricitätsleitung in Electrolyten," published in Poggendorff's *Annalen*, ci. p. 338, 1857 †.

As it forms the basis of the modern dissociation theory, any attempt to comprehend the latter would properly begin with a study of the former. In discussing the views of Clausius we may conveniently consider, first, the reasons given for the inadequacy of the then commonly accepted theory of Grotthus, and, second, the probability of the new hypothesis put forward in its place.

Clausius objects to the Grotthus theory chiefly for two reasons. He explains in detail in § 5 that considering, for instance, the anode, the negative part-molecules are here retained while their positive partners decompose the next stratum of adjacent molecules, and so on; and that this results in a surplus of positive part-molecules implying a surplus of positive electricity in the liquid, which, as he has previously shown, is inadmissible. In like manner the action at the cathode would result in a surplus of negative electricity equally inadmissible.

Now, though it be admitted that this reasoning may be correct when applied to each pole separately, it fails, I think, when both are taken together. The two charges of opposite sign would then combine and, in fact, may be said to constitute the current produced.

In other words, the Grotthus molecular chains do not end in the interior or at the free surface of the electrolyte, but only at the electrodes, so that the action may be said to be here reciprocal and complete.

The second objection to the older hypothesis (§ 6) is

\* Communicated by the Electrolysis Committee of the British Association, having been read at the meeting of the Association in August 1891.

† Also *Phil. Mag.* [4] xv. p. 94.

practically that, according to it, electrolytes could not obey Ohm's law for a gradually increasing electromotive force; whereas according to Clausius they do obey Ohm's law if, as is carefully pointed out in a footnote, we consider only the force acting in the interior of the electrolyte, and not that at the electrodes, where the products of decomposition are separated and polarization has to be overcome.

But we may ask, Is this an admissible limitation? Is it allowable, when considering a process of decomposition, to expressly leave out of account the only parts of the mechanism where decomposition visibly occurs, viz. the electrodes? If the whole system be taken into consideration, electrolytes do not of course obey Ohm's law, and a more or less abrupt rise in the ratio of current to E.M.F. does take place when a gradually increasing E.M.F. reaches a point which, speaking generally, has a relation to the heat of combination of the decomposing body\*.

Below this point the current which accompanies smaller E.M.F.'s is, no doubt, accompanied by decomposition; but of what? Can it be shown, for instance, that when a minute E.M.F. produces a continuous current through HCl solution, it decomposes HCl or any other substance of considerable heat of formation; and that the current is not more probably conducted by decomposition of impurities, hydrates or complex molecules, whose parts have minute attractions for each other; or that, supposing HCl is decomposed, the action is not masked by the well-known secondary effect of dissolved oxygen or other "depolarizer."

On considering the whole electrolytic system, then, this second objection must also be put aside, and in so far Clausius cannot be said to have shown the need of a new hypothesis †.

The probability of the new hypothesis proposed by Clausius, as described in §§ 7 and 8, may, however, be considered. In §7 we are asked, without any previous explanation, to consider a positive part-molecule, and to assume that its electric state remains the same after separation from the complete molecule. This is the first reference in the paper to such a single separate electrified part-molecule. It is described as moving about among the other complete molecules; but no explanation appears to be given before as to how such a thing came to exist. It is explained, however, in detail that these

\* This was illustrated by a set of curves for the decomposition of various electrolytes given by the present author, *Phil. Mag.* June 1891.

† In pointing out the invalidity of these objections, it is not intended to acquiesce in the pure Grotthus theory. The modification of it put forward by Faraday is probably much nearer the truth.

dissociated part-molecules in the electrolyte are normally engaged in ousting other part-molecules from their partners by a process of exchange which, when directed by the attraction of the positive and negative poles, constitutes electrolysis; the dissociated part-molecules finally becoming attracted to their respective poles and evolved there in the free state\*.

It is evident, however, that by this process the original number of dissociated part-molecules is not increased, and therefore must soon become exhausted at the electrodes by the action described, after which conduction would cease. Yet it is evidently necessary for continuous conduction that a steady average proportion of dissociated part-molecules be supplied.

A process which would provide for at least some fresh dissociation of whole molecules is described in the third paragraph of § 7 as one that may occur, but does not seem to be recognized as a necessity. It is assumed that in the course of the heat-vibrations among the molecules the negative part of one whole molecule may come so close to the positive of another as to combine with it, leaving the former partners of each free. (It would seem more likely that if two partners combined, the other two would combine also, and would not be left free to move apart against the attraction of their supposed electric charges.)

Granting, however, for the moment that dissociation of this kind may occur, and that thereby a certain steady average proportion of molecules in the liquid is kept dissociated, and that these are supposed to be led away in opposite directions by the electric force acting on their supposed electric charges. Now, if we consider any given volume of the electrolyte, this abduction of molecules would destroy the balance between the associated and dissociated molecules, and therefore would lead to fresh dissociation in order to restore it. This dissociation requires a considerable amount of energy, whereas the deportation of the molecules involves a very small amount of electric work done; thus we should have the heat of the fluid used up to produce energy of a mechanically utilizable type, in contradiction to the law of entropy and also in disagreement with experimental observation.

\* It is, of course, very well known that Faraday objected to calling substances "*electropositive* or *electronegative* according as they go under the supposed influence of a direct attraction to the positive or negative pole," and considered these terms "much too significant" (Exp. Res. i. p. 197).

Hittorf also states as a conclusion from his research on the migration of ions, "Es ist ganz falsch den Polen besondere Anziehungs- oder Abstossungskräfte zu ertheilen" (Pogg. Ann. ciii. p. 20, 1858).



On the other hand, if the work done by the current, in separating from any electrolyte certain substances, is the equivalent of the heat evolved by the recombination of those substances, it seems simpler to assume that the work is directly applied to produce decomposition at the electrodes.

The hypothesis of molecular interchange as proposed by Williamson to explain the process of etherification is quoted by Clausius in §10 in support of his theory; but Williamson's process was purely one of molecular interchange between the partners of whole molecules, no part-molecule separating off till in the act of combining with a new partner. It is limited to this, and there is no mention of separate part-molecules, dissociation theories, or so-called free ions. Therefore, though the dissociation theory has been frequently referred to as the Williamson-Clausius hypothesis, it is not supported in any way by Williamson's paper.

From these considerations it would appear that both the necessity for and the probability of the hypothesis put forward by Clausius are very doubtful.

Turning now to more modern views, I have already pointed out in the 'Electrician' for April 19, 1889, that an experiment considered by Prof. Ostwald as serving to remove the last doubts as to the validity of the assumption of free electrically-charged atoms of chlorine and potassium\*, is of a purely negative kind, and throws no new light on the subject at all.

An experiment is described by the same author in the *Zeitschrift für physikalische Chemie*, vi. p. 72, which on examination appears to be of a similar kind. It is given as evidence touching the assumption that a semi-permeable wall, interposed between two electrolytes in the path of a current, will permit certain ions to pass but not others; and it is further intended to decide as to what will happen under these circumstances. It is assumed that in such a case either no current will pass, or else the ions must give up their charge through the semi-permeable wall, which then acts as a metallic electrode.

Briefly, the experiment is as follows:—Two vessels containing copper-sulphate solution were joined by a siphon full of potassium-ferrocyanide solution, its ends being closed by parchment-paper. A deposit of copper ferrocyanide formed in the pores of the paper. This arrangement was placed in circuit with a battery and galvanometer. A current of 40°

\* 'Outlines of General Chemistry,' p. 275.

was observed, which decreased, at first rapidly, and in about a quarter of an hour became constant at  $10^3$ . When the battery was cut out of the circuit there was a strong secondary current, and on dismantling the apparatus, it was found that copper had been deposited on the parchment-paper in that vessel containing the positive pole of the battery.

From these observations it was concluded that the positively charged copper ions, not being able to pass the partition, gave up their electricity in order to deposit in the metallic form. Certain electrochemical actions are described in detail as having occurred at the other portions of the circuit, such as the passage of potassium atoms through the other partition, but apparently no attempt was made to ascertain if they actually took place. One has a right to expect that some evidence of their occurrence should be given, but none appears. Simply the conclusion is drawn that the foregoing appears to show the correctness of the above-mentioned proposition, that the semi-permeable walls are for certain ions permeable, and for others not.

But it will, I think, be admitted that in the absence of any investigation by analysis or otherwise of the actual products at the porous walls, the phenomena actually described might arise from a certain degree of conductivity in the matter precipitated in the parchment-paper. In fact, if the parchment-paper were replaced by platinum sheet with either a small amount of any kind of porosity or none at all, phenomena the same as, or similar to, those actually observed would occur, *i. e.* the initial decrease of current, the secondary current, and the deposit of metallic copper.

It remained, then, to test the precipitate for conductivity. I prepared it by adding potassium-ferrocyanide solution to excess of copper-sulphate solution, filtered off and washed the red-brown precipitate (which is said to strongly retain potassium ferrocyanide, together with the copper salt), and dried it in the air without heating.

Into one limb of a small U-tube, about 9 millim. in diameter, was dropped a short piece of carbon rod of nearly the same diameter as the tube and connected to a platinum wire passing up the other limb for connexion to battery and galvanometer. On the end of the carbon was spread a layer of the precipitate about 1 millim. thick. The whole was then placed in a small glass jar containing strong sulphuric acid, and closed by a paraffin plug through which passed a carbon rod that could be brought down on the precipitate. After standing eight days to dry the precipitate and glass surfaces, the upper carbon was lowered into the tube, but not in contact with the precipitate,

and the arrangement put in circuit with two cells and a reflecting-galvanometer. No deflexion ensued; but as soon as the upper carbon was pressed down on the precipitate, there was a deflexion of 429 divisions. To estimate roughly the resistance of the layer of precipitate, a resistance of 10,000 ohms was now interposed. This reduced the deflexion to 426, indicating a resistance of about three quarters of a megohm.

On cutting out the battery there was a distinct secondary current. This secondary current would go to show that the precipitate was a conductor of the second order, and therefore perhaps unlikely to act as a metallic diaphragm. It was therefore necessary to examine the nature of its conductivity more closely; and since the precipitate prepared as described is complicated by the presence of potassium ferrocyanide, I prepared a fresh portion of cupric ferrocyanide by the method of Ramelsberg for obtaining the pure substance\*. I mixed the aqueous solutions of hydroferrocyanic acid and pure copper sulphate, filtered out and well washed the precipitate, dried it *in vacuo* over sulphuric acid, and tested it in the same apparatus as before. Its resistance appeared to be about half as much again as that of the first precipitate. With an E.M.F. of about .01 volt it conducted sensibly; with three volts it gave a deflexion of about 700 divisions; and when this latter current had passed for six minutes, on removing the battery the only evidence of polarization was a mere quivering of the index over about two divisions on making contact.

There would appear to be no doubt, therefore, that cupric ferrocyanide is a conductor of the first order, although of somewhat high resistance; and the phenomena of Prof. Ostwald's experiment (so far as one can judge from the merely qualitative data given) may be explainable on a very simple hypothesis without having to attribute them distinctly or solely to any semi-permeability in the partition.

The polarization observed with the first precipitate may be due to impurity, perhaps to the mixture of potassium ferrocyanide. Its persistence, notwithstanding the short-circuiting by the conducting cupric ferrocyanide, may easily be due to the very high resistance of the latter.

In any case, however, the conductivity of cupric ferrocyanide must evidently be taken into account in all the experiments in which it takes a part. In those on osmotic pressure for instance, where a porous partition containing a deposit of this salt in its pores is interposed between water

\* Pogg. Ann. lxxiv. p. 65, 1848.

and a salt solution, we may have in each pore a small voltaic circuit composed of the cupric ferrocyanide as metallic conductor, and the two liquids as electrolytes. That very unusual phenomena may arise in a minute circuit of this kind is already shown by the copper-zinc couple of Gladstone and Tribe. But whatever the actual process may be in this osmotic-pressure experiment, it is evident there is more to be considered than the mere smallness of the pores.

In the B. A. Report, 1890, p. 333, Prof. Ostwald concludes that one consequence of the dissociation hypothesis is that "in general water must show against every electrolytic solution the potential of the faster ion;" and that this is confirmed by the experiments of Nernst and of Planck at references given. In Planck's paper he does not appear to have made any experiments himself, and those of other authors referred to were carried out by means of metallic poles immersed in the liquids, and so introducing the unknown quantity of metal-liquid contacts. The experiments of Nernst appear to have the same defect, and, in addition, to refer only to circuits containing three or more liquid contacts, and cannot give any definite information about individual contacts.

This evidence is therefore also of a purely indecisive character.

In the same Report, p. 335, the same author states that "according to Faraday's law all chemically equivalent amounts of positive and negative ions are charged with equal amounts of electricity." One could wish that Prof. Ostwald had given a reference to Faraday's statement of this "law."

In the *Philosophical Magazine* for August 1891, Prof. Ostwald describes some cases of what he terms chemical action at a distance in the following form of experiment. He points out that while pure zinc is scarcely acted on by a solution of common salt alone, yet in a circuit consisting of zinc, salt solution, hydrochloric-acid solution, platinum, the zinc dissolves when connected to the platinum, *i. e.* by the action at a distance of the acid. There is certainly, as Prof. Ostwald partly admits, nothing new in this form of experiment. It is as old and familiar at least as the Grove's battery, and the action is commonly explained on the old theory of consecutive molecular interchanges coupled with considerations of the thermo-chemical relations of the acting bodies. Prof. Ostwald brings it out as speaking forcibly for the value of the "free ion" theory, assuming that the action depends primarily on the passing into the solution of positively charged atoms from the zinc, but states that it cannot be explained how the charging takes place, or in what it

consists. Are we, then, any nearer an explanation of the phenomena than in the older theory, seeing it does not appear that there is anything in this form of experiment which supports the free ion theory *in preference* to the older one?

Prof. Ostwald here states that zinc [and by implication any other metal acted on by an electrolyte] becomes negative to the electrolyte, while, according to his experiments with mercury-dropping electrodes\*, the metals were considered positive. In a criticism of these mercury-dropping experiments already published †, I pointed out that the latter conclusion, in the case of mercury when thus acted on, was probably incorrect, and that, if so, the hypothesis on which the results were explained was erroneous. It would be interesting to know if the two theories can be reconciled.

In conclusion it will, I hope, be apprehended that the above criticisms are offered, not to prove or disprove any particular theory, but rather to point out that in support of certain theories there is being advanced a quantity of evidence that appears entirely indecisive. So long as no *experimentum crucis* can be pointed out, and all the theories explain known experimental results, we advance no nearer a real knowledge of the truth, and it seems a pity (supposing the dissociation theory contain any truth) to overweight it at present with evidence the inapplicability of which must be continually discouraging to the student.

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## IX. *On a New Method for obtaining a Constant Temperature.*

By MR. HENRY CREW, *Instructor in Physics in Haverford College* ‡.

THE following work was suggested by an attempt on the part of the writer to determine the coefficient of expansion of water by the areometric method of Matthiessen, using, instead of a solid piece of glass, the hollow glass bulb of a weight thermometer.

It was very soon found, however, that the errors introduced by temperature-variation of the water in which the bulb was weighed far surpassed all other errors involved.

The problem which must be solved, before this or any other method yet devised is available for accurate work, is to produce, throughout a certain limited space, a constant temperature, and to maintain this temperature for a time sufficient

\* *Zeitschrift für physikalische Chemie*, i. p. 583, 1887.

† *Phil. Mag.* [5] xxvii. p. 390, 1889.

‡ Communicated by the Author.

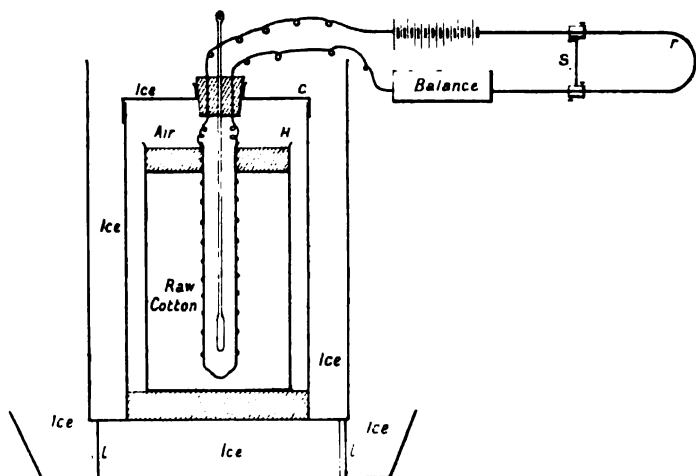
for one to make his observations. The writer offers the following solution :—

Take the body within which it is desired to maintain a constant temperature, and wrap it very closely with a fine covered wire having a high specific resistance. The wire should not be of iron, or any substance which is liable to suffer large permanent changes of resistance by oxidation or heat. The body having been wrapped as completely, as closely, and as uniformly as possible, a constant electric current is now passed through it. By this means can be practically developed the same amount of heat per second over every unit of surface of the body.

If now the body is surrounded by another and larger surface of lower constant temperature, the amount of heat which is radiated to the latter per second will keep on increasing until it is just equal to the amount produced per second by the electric current.

Between the inner heating wall and the outer cooling surface we shall then realize the condition of steady flow, while *within* the heating surface, thus held at a practically constant temperature, we shall have exceedingly small variations in the reading of the thermometer.

An experimental test of the method was made as follows:—



A cylindrical copper vessel C about 10 inches in diameter, and having double walls, was mounted on three legs, two of which (*l*, *l*) are shown in the figure. C can thus be packed in a cylindrical wall of ice.

The whole is then set in a small dish-pan, which allows

ice to be easily packed under the bottom of C. If an ordinary double bottom be used it will be found difficult to keep ice there, and the temperature of the water is liable to rise to  $4^{\circ}$  C.

Within C is placed another copper vessel H, containing whatever is to be heated to constant temperature. In this experiment I used a large glass test-tube wrapped with No. 22 German-silver wire. Some cork feet were waxed on to the bottom of H, and the test-tube was suspended in H by means of a cork top. Cork in the figure is indicated by diagonal shading.

A little raw cotton placed about the test-tube in H will stop convection-currents and much improve the steadiness of the temperature.

On C is next placed a metallic cover through which the terminals of the wire wrapping are led out and connected to the battery. This metal cap is covered with crushed ice, and the whole inside region is thus surrounded by a wall at zero.

The test-tube was filled with water whose temperature was measured with a sensitive Baudin thermometer on which the degrees (Centigrade) were 10 millim. long; so that with a telescope there was no difficulty in reading to  $\frac{1}{100}$  of a degree.

In series with the storage battery (in this case 12 cells) is placed a loop, *r*, of German-silver wire on which are strung two wire connectors. A copper shunt, *s*, soldered across these two connectors, as in the figure, makes of the whole a simple and excellent rheostat by means of which changes in the E.M.F. of the batteries, or temperature changes in the resistance of any part of the circuit, may be compensated.

A duplicate slider, parallel to *s*, should be added in order that one may be clamped while the other is moved, thus never breaking the current.

A simple rheostat, devised by Mr. C. H. Bedall, and occupying much smaller space, is made by ploughing a number of longitudinal grooves in a piece of  $\frac{7}{8}$  stuff and connecting by U-shaped copper connectors. These grooves are then filled with mercury, and the resistance varied by sliding the connectors.

As a source of constant current I have used Julien storage-cells, and find that they leave little to be desired.

One does not need a large current even for the production of comparatively high temperatures; for the final temperature of the enclosed space increases as well with the thermal conductivity of the packing between the hot and cold walls

as with the current strength, or the resistance of the wrapping, the steady flow of heat obeying Ohm's law.

For the recognition of a constant current one cannot use an ordinary tangent-galvanometer, since, while variations in the *direction* of  $H$  can be eliminated by commuting the current through the galvanometer, the variations in the *intensity* of  $H$  cannot be so eliminated. Neither is a D'Arsonval galvanometer available; for there is a time-variation in the rigidity of the wire suspension, and a temperature-variation in the field of the permanent magnet. Not only so, but such an instrument must be used with a shunt, and unless the shunt has the same temperature-coefficient as the suspension-wire and coil of the galvanometer, the *shunt ratio will vary* with the temperature. However, if one has no better instrument at his disposal fair results may be obtained with this. A Thomson centiampere or milliampere balance, being independent of thermal and magnetic changes, and needing no shunt for ordinary purposes, is an ideal instrument for this work.

The rheostat,  $r$ , should be placed immediately in front of it for convenience.

An additional convenience is obtained by placing a relatively small resistance in series with the Thomson balance, so arranged that it can be shunted out at will. In this way the current can be temporarily increased. Otherwise it will take a long time for the condition of steady flow to be reached.

A temporary increase of this kind is what is meant, in the observations which follow, by the note, "*current temporarily increased.*"

### Observation I.

Time of Obs.		Reading of Thermometer.	Current on D'Arsonval Galvanometer.
h	m		div.
3	10	38.10	8.350
3	20	38.10	"
Current interrupted.			
3	47	37.87	8.350
3	57	37.86	"
4	05	37.87	"
4	15	37.87	"
4	25	37.87	"
4	31	37.87	"
4	49	37.875	"



## Observation II.

Time of Obs.		Reading of Thermometer.	Current on Thomson Balance.
h	m		centiamperes.
7	04	25.37	36.00
7	16	25.38	"
Current temporarily increased.			
7	29	25.57	36.00
7	33	25.57	"
7	53	25.57	"
8	03	25.575	"
8	13	25.58	"
8	20	25.585	"
Current temporarily increased.			
8	29	25.67	36.00
8	33	25.67	"
8	43	25.67	"
8	53	25.67	"
9	03	25.67	"
9	13	25.675	"
9	23	25.68	"
9	33	25.685	"

These observations were made during the past summer in the Physical Laboratory of Haverford College.

From the first set it will be seen that the temperature was held constant within  $\frac{1}{100}$  of a degree for three quarters of an hour; in this case no cotton packing was used.

In the second set it will be observed that the condition of steady flow has not quite been reached, for the temperature continues to rise slowly. Nevertheless, there are two separate intervals of more than 40 minutes each, during which the variation does not exceed  $\frac{1}{100}$  of a degree.

I regret having had to leave the laboratory before I could make further experiments, for I feel confident the method is able to give much greater constancy.

Its chief advantages are that it can be applied to a vessel of almost any shape in almost any position. This feature makes it especially valuable for the determination of coefficients of expansion by the method of Boguski described in the *Zeitschrift f. phys. Chem.* ii. p. 482; in fact, it was for use in this problem that the method was devised.

Unlike the method of vapour baths, it will give any temperature desired. This temperature can be obtained by trial very quickly, without previous experiment, or the calorimeter can be calibrated and the ampere-balance set for the correct current at once.

Lick Observatory.  
October 1891.

X. *On the Existence of a Compound of Gold and Tin.*

By A. P. LAURIE, M.A.\*

**M**ATTHIESSEN, in his classical researches on alloys, divides the metals into three classes—namely, those which when melted together seem to be merely mixed; secondly, those in which a complete change of properties takes place on the addition of a very small quantity of another metal; and, lastly, those between which something of the nature of chemical combination seems to take place.

He finds, on determining the electric conductivity of alloys belonging to these different classes, that in the case of the first group the curve of conductivity is a straight line, that in the case of the second, and by far the largest group, the curve of conductivity resembles a U; but that in the case of the third group the conductivity abruptly rises at some point and then falls again, such discontinuities, according to Matthiessen, indicating the existence of compounds formed between the two metals.

It is, I think, open to question whether many of the alloys placed by Matthiessen in the second group should not be removed to the third group, as in some instances, owing to the difficulties of the research, he has not made a sufficient number of observations to prove the absence of a rapid rise and fall in the course of the conductivity-curve.

This view is confirmed by the experiments made by Prof. Roberts-Austen on the copper-tin alloys. On examining the conductivity of these alloys by means of the induction-balance, he found that such a discontinuity existed lying between two observations of Matthiessen's, and which he consequently had never suspected—thus removing these metals into the class which combine with each other.

Nobody, as far as I am aware, has attempted the task of redetermining the electric conductivity of the alloys as a whole; and it is therefore, I think, of some interest to search for these compounds by a new method, and thus throw fresh light on the results obtained by a determination of the physical properties of the alloys.

The method I have adopted has been already described in former papers.

Briefly it is based on the fact that if in, let us say, a Daniell's cell the zinc plate is replaced by a copper plate, so as to reduce the E.M.F. practically to zero, and if then a very minute portion of zinc be attached to the copper plate,

\* Communicated by the Author.

the zinc will polarize the whole surface of the copper, and the cell will give very nearly the same deflexion on an electrometer as a Daniell's cell.

We have here, then, a delicate method for detecting the presence of very small quantities of a more positive metal when merely mixed with a more negative metal.

If, however, these two metals have entered into combination with the evolution of heat, energy must be absorbed in the cell to break down this compound, and we should expect the E.M.F. to be correspondingly lowered.

Let us now suppose that using the same Daniell's cell we replace the zinc plate by an alloy formed by melting together copper and zinc, for instance a piece of ordinary brass wire. We find that this brass wire behaves like a piece of copper in the cell, that apparently the zinc it contains is not free to enter into combination.

On now making up a series of alloys, each containing more zinc than the last, and testing their E.M.F. in the cell, an alloy is at last reached which gives almost the same E.M.F. as zinc, while the alloy before it behaved like copper in the cell, though only containing 2 or 3 per cent. less of the more positive metal.

We have evidently, then, just passed over the alloy containing exactly the right proportions of the two metals to form the compound, and are now dealing with alloys which consist of the compound mixed with an excess of free zinc, while all the alloys before that point had consisted of the compound mixed with an excess of free copper.

In the case of alloys, however, where the metals are merely mixed, the introduction of a very small percentage of the more positive metal would at once be indicated by the electrometer.

In this way I have examined the alloys formed between the metals tin, zinc, lead, and cadmium, and the results have already been published. In the case of these alloys, a very small quantity of the more positive metal at once caused an increase of E.M.F., thus confirming Matthiessen's result that these alloys are merely mixtures of the two metals one with the other. In the case, however, of the copper-zinc and copper-tin alloys, combination had evidently taken place, the rise of E.M.F. of the copper-tin series taking place at the same composition at which the maximum point of the curve of conductivity occurs, as redetermined by Prof. Roberts-Austen. Whether a redetermination of the conductivity of the copper-zinc alloys would show a similar discontinuity agreeing with the point at which the rise of E.M.F. occurs remains to be seen.

Having thus dealt with alloys occurring in Matthiessen's first two groups, it seemed of interest to examine next an alloy in which he believed chemical combination to have taken place, and I have therefore selected the gold-tin alloys as most suitable for this purpose.

Matthiessen's conductivity-curve for these alloys resembles a **W** in shape, and he suggests that there are three compounds formed by these metals, one corresponding to the maximum point, and two to the minimum points of the curve. To these compounds he gives the formulæ  $\text{Au}_4\text{Sn}$ ,  $\text{AuSn}$ , and  $\text{Au}_2\text{Sn}$ , respectively\*. It remains to be seen what fresh light the new method throws upon these conclusions.

With a view to these experiments I obtained some precipitated gold and some of their finest grain tin from Messrs. Johnson and Matthey, and made up with these a series of gold-tin alloys by melting the metals in a clay tobacco-pipe, and after thorough mixing drawing the melted metal into the stem. The alloys so obtained were white and brittle, the only one having a slightly yellow colour being the last of the series, containing 10 per cent. of tin. The percentage composition was calculated from the weights of each metal taken. This was found sufficiently accurate, and was checked in the case of one alloy, as will be presently explained, by an assay which Prof. Roberts-Austen kindly had made for me at the Mint. The result of the assay only differed by .2 per cent. from the composition calculated from the weights of metal taken.

The alloys having been prepared, a small voltaic cell was arranged, consisting of a solution of stannic chloride in the outer cell, prepared by passing chlorine into stannous chloride, and a solution of gold chloride in the inner cell, in which was immersed a plate of pure gold. A brass clip tipped with platinum and connected to mercury poles in a paraffin block was used to hold the little rods of alloys. Each rod of alloy was carefully cleaned with a fresh piece of glass-paper just before being immersed in the cell.

The measurements were made with a Thomson's quadrant-electrometer and checked against a standard Latimer-Clarke cell.

Two or three peculiarities showed themselves with this cell which I have not observed in the case of my experiments with other alloys. In the first place, a considerable deflexion was obtained between two plates of gold, one in the outer and one in the inner cell, apparently owing to an E.M.F. between

\* Dr. A. Matthiessen on "The Electric Conducting-power of Alloys," *Philosophical Transactions*, 1860, vol. cl., Part I., p. 187, Tin-Gold Series.

the two liquids. Then, on immersing the first alloy, containing 10 per cent. of tin, a further rise of E.M.F. was obtained, showing quite a marked difference between the gold and the alloy. In other cases where a compound has been found in the series, very little, if any, rise of E.M.F. has taken place until that compound has been passed. This seems to indicate that in the case of these alloys the energy required to decompose the compound is not so great as to reduce the E.M.F. of the cell to that obtained with gold alone.

Another peculiarity of a more objectionable kind was the fluctuations in the readings taken on different days. These were small and did not affect the relative positions of the alloys one to another, all rising or falling together in E.M.F., and was doubtless due to changes in the unstable solutions used. The results obtained are given in the following Table:—

Weight of Metals taken.	Percentage of Tin in Alloy.	E.M.F. in volts.
Gold—Gold .....	.....	·667
Gold 1·803 grms. Tin ·202 grms....	10·07	·923
Gold 2·000 grms. Tin ·602 grms....	23·1	·932
Gold 2·002 grms. Tin ·704 grms....	26·01	·923
Gold 2·000 grms. Tin ·800 grms....	28·5	·941
Gold 1·303 grms. Tin ·700 grms....	34·9	·932
Gold 1·284 grms. Tin ·722 grms....	35·9	·950
Gold 1·201 grms. Tin ·801 grms....	40·0	1·215
Gold 3·001 grms. Tin 3·001 grms....	50	1·279
Gold—Tin .....	.....	1·425

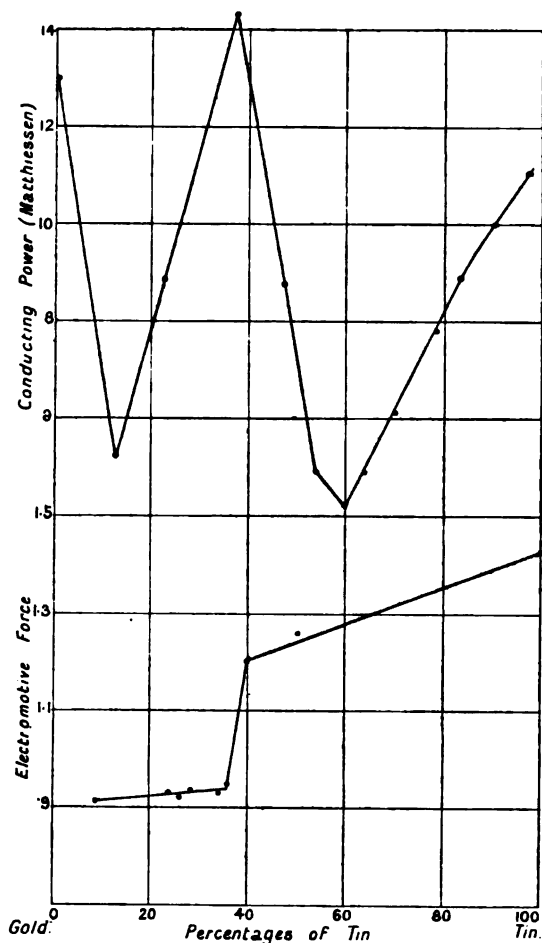
On looking at this Table it will be noticed that the readings remain nearly the same from the first alloy up to the one which contains 35·9 per cent. of tin; but in passing from that to the alloy containing 40 per cent. of tin, a rapid rise in the E.M.F. takes place. From this point up to pure tin the E.M.F. only rises ·21 volt, the curve being approximately a straight line. This shows that between these two alloys an alloy exists containing the metals in the right proportion to form a compound, and that on reaching the alloy of 40 per cent. of tin the compound has been passed and free tin is present. In order to push this point closer home I prepared an alloy which is not given in the Table and which I made up to contain 38·1 per cent. of tin. This alloy was assayed at the Mint, with the following result:—

Gold ..... 61·7 per cent.  
 Tin ..... 38·3     "     by difference.

100·0

98 *On the Existence of a Compound of Gold and Tin.*

This alloy was remarkably brittle, so brittle that I could only prepare it in short pieces. On testing the E.M.F. of small pieces of this alloy they behaved in a curious way, some of them giving the E.M.F. 1.2 volt, others the E.M.F. .95 volt,



and others intermediate numbers. Fresh sand-papering the surface also affected the results. This behaviour is just what might be expected to happen on testing an alloy containing a very small excess of free tin scattered through the compound and sometimes absent altogether, and sometimes eaten from the surface by local action. Evidently, then, the compound had just been passed over. On now comparing these results with

### *Variation in the Density of Water with the Temperature.* 99

those obtained by Matthiessen, we find that he fixes the maximum point of his curve at an alloy containing 37 per cent. of tin. This number agrees pretty closely with the formula  $\text{AuSn}$  if we take tin as having an atomic weight of 118, and gold as having an atomic weight of 197. The formula, then,  $\text{AuSn}$ , the maximum point of the electric conductivity-curve, and the point where the E.M.F. abruptly rises, lie between the alloys containing 36 per cent. and 38 per cent. respectively of tin. This method, then, confirms the existence of one of Matthiessen's supposed compounds, but has not confirmed the existence of the other two. It agrees, however, with the results obtained with the copper-tin alloys, and taken in conjunction with them shows that the point of maximum conductivity is the point where a compound exists. This does not seem an unreasonable result. Compounds of the formula  $\text{Au}_4\text{Sn}$  and  $\text{Au}_3\text{Sn}_5$  are not very probable. Furthermore, the most common form for the curve of electric conductivity to take in the case of metals not combining is a U. If we regard the compound  $\text{AuSn}$  as practically a new metal of fairly good conductivity, we should expect two regions of depression between  $\text{AuSn}$  and gold, and between  $\text{AuSn}$  and tin to make the results correspond to those usually obtained. But we may derive a further conclusion from the E.M.F. measurements in the case of these alloys. The change in E.M.F. in passing over the compound amounts to .25 volt. Now this is a measure of the energy absorbed in the cell in decomposing the compound and may, therefore, be taken as an approximate measure of the heat of formation of the compound itself.

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### *XI. The Variation in the Density of Water with the Temperature.* By D. MENDELKEFF\*.

THE expansion of water with change of temperature, although presenting great scientific interest, both for the comprehension of the action of heat upon matter and also for many experimental investigations, cannot yet be considered as elucidated in its theoretical aspect nor sufficiently worked out experimentally. It will be seen from Tables I. and II. that in the best existing determinations, and after the introduction of possible corrections †, we encounter discrepancies which,

\* Translated by G. Kamensky. Communicated by Prof. Crum Brown, F.R.S.

† For instance, possible corrections for the value of the true coefficient of expansion of mercury, for the readings of the mercury thermometer, for weighing in air, for the increase of the expansion of the vessel with a rise of temperature, &c. Further on I consider certain of these correc-

even for ordinary temperatures, exceed hundred-thousandths \* while the accuracy of gravimetric and volumetric measurements can now be carried to millionths.

The publication of the present paper previous to my having been able to undertake a series of fresh and properly instituted determinations of the expansion of water, is accounted for by the fact that the collation and elaboration of the existing data referring to this subject has led me to the following somewhat simple expression :—

$$S_t = 1 - \frac{(t-4)^2}{(A+t)(B-t)C}, \dots \dots (1)$$

which embraces all that is known for the variation of the density of water ( $S_t$ ) between  $-10^\circ \text{C}$  and  $+200^\circ \text{C}$  † with all the accuracy now attainable. A general expression for the variation of the density of water, while presenting a means for

tions in detail. I have introduced some of them into the existing data of many observers, but I do not give the results thus obtained in this article, because in the first place I wish to preserve the original results of the experimenters, knowing that the greatest interest is always attached to them, and in the second place because many of these corrections are of doubtful value, unless they are made by the observers themselves. When studying the literature of the subject, it becomes a matter of regret that the majority of observers do not give their original experimental numbers (for example, the apparent volumes or weights of water). If these were known, it would be easier to introduce the necessary corrections and to form an estimate of the magnitude of the errors inherent in the figures thus given.

\* For example, at  $25^\circ$  the volume of water, according to Jolly, is equal to 1.002856; according to Matthiessen it is 1.002982. The first number approaches to the values given by Rosetti, Hagen, and others; the second is nearer to Despretz's determination.

† In his admirable determinations of the expansion of water from  $100^\circ$  to  $200^\circ$ , Hirn plainly states that at these temperatures the expansion of water is expressed differently and more simply than at lower temperatures. Kopp and the majority of investigators give empirical expressions (by interpolation) for the expansion of water for only small variations of temperature, for instance from  $75^\circ$  to  $100^\circ$ , their endeavours to obtain a general expression, comprising the whole range of volumes from  $0^\circ$  to  $100^\circ$ , having been fruitless. Frankenheim (Pogg. Ann. 1852, lxxxvi. p. 463), in undertaking the great labour of making a series of fresh calculations for all the experimental data of Pierre, had in view to seek out a general expression ("Ausdruck des Naturgesetzes") answering to the "conflict between heat and cohesion which evinces itself in the variation of the density of water," but was unsuccessful in finding a general algebraical expression for the dependence which is here concealed. He concludes his memoir with the words "Das Problem ist noch ungelöst." From this we see that the great importance of having a simple general algebraical expression for the expansion of water with a rise of temperature was long since recognized by many scientists.



working up experimental data, may also have a certain theoretical significance, inasmuch as it may assist in explaining the general law of the expansion of liquids \*. For all liquids except water the rate of change of the density with the temperature (*i. e.* the differential coefficient  $\frac{ds}{dt}$ ) varies but little, either rising or falling slightly with considerable variations of temperature ; for example :—

		Amyl alcohol.	Sulphuric acid (93½ p.c.).	Phosphorus tribromide.	Mercury.
$S_0 =$		0.8248	1.8525	2.92311	13.5956
$\frac{ds}{dt}$ at	0° ...	—0.00076	—0.00106	—0.00244	—0.002447
	25° ...	—0.00077	—0.00102	—0.00245	—0.002439
	50° ...	—0.00080	—0.00099	—0.00245	—0.002431
	100° ...	—0.00094	—0.00092	—0.00246	—0.002415
According to	Kopp (1855).		Kremers (1863).	Thorpe (1880).	Regnault.

In the case of water, on the other hand, the differential coefficient  $\frac{ds}{dt}$  not only changes its sign at 4°, but in general varies with extraordinary rapidity, even (judging from Hirn's data, 1867) at temperatures far removed from 0°, above 100°:—

	0°.	25°.	50°.	100°.	160°.	200°.
$10^5 \frac{ds}{dt} =$	+6	—25	—45	—72	—100	—120

Although I do not desire here to touch upon the question of a first approximation towards the general law of the expansion of liquids, I consider it necessary to state that the

\* In the Journal of the Russian Physico-Chem. Soc. for 1884 (and also in the Journal of the Chem. Soc. London, 1884), I stated that the expansion of liquids may be approximately expressed (at a point far removed from their passage into another state and within the range of the ordinary accuracy of determinations) by an equation of the form  $S_t = S_0(1 - kt)$ ; and although in various quarters doubts were entertained as to the generality of such a law (especially by Avenarius and Grimaldi), on the other hand, not less weighty proofs of its applicability were brought forward (notably by Thorpe and Rücker, Kraewicz and Konovaloff); so that the question of a general law for the expansion of liquids must be considered as having just entered upon its first phases of historical development. Just as when elaborating my first article (Journal of the Russ. Physico-Chem. Soc. 1884, p. 7), I then considered the question of the expansion of water as unique, and as requiring special determination, so now I maintain that the working out of this problem will advance the very idea of the general law of the expansion of liquids. I trust to return to this subject shortly.

aspect of formula No. 1 bears a certain relation to this subject, as will be seen from the method by which I arrived at it.

In order to obtain an expression fulfilling the condition that the density of water at  $4^{\circ}$  be taken as  $=1$ , it was necessary in the empirical formula

$$S_t = a + bt + ct^2 + dt^3 + \dots$$

to take  $a=1$  and to make the sum of all the remaining members of the series divisible by  $(t-4)$ . But in order to comply with the fact that the density of water attains a maximum at  $4^{\circ}$ , it was necessary to admit that the remaining members are once more divisible by  $(t-4)$ , because then, when  $t=4$ , the differential coefficient is equal to zero\*. Therefore the formula

$$S_t = 1 - (t-4)^2 F(t), \dots (2)$$

where  $F(t) > 0$  and  $< 1$ , should be taken. Having determined the values of  $F(t)$  or the magnitudes  $(1-S_t)/(t-4)^2$  from the aggregate of existing data, I became convinced from

\* As far as I know (from a notice in *Pogg. Ann.* 1853, xc. p. 628) Hassler, in America in 1832, was the first to apply an expression of the form

$$S_t = S_0 - A(t-t_m) - B(t-t_m)^2,$$

where  $t_m$  is the temperature of maximum density, for calculating the density of water. The necessity for discarding the term  $(t-t_m)$  in the first degree, and for taking it only in the second degree, was already recognized by Miller (*Phil. Trans.* 1856), and is repeated by Hagen and Rosetti. But these observers, in their calculations for the expansion of water according to the formula

$$S_t = 1 - (t-t_m)^2 A + B(t-t_m)^{2+n} - C(t-t_m)^{2+k},$$

&c., have up till now always only adopted such functions where  $t$  invariably has a positive exponent, i. e. only enters into the numerator; whereas I have become convinced that formulæ of this kind satisfy the aggregate of known facts only when taken with a large number of terms, even if fractional indices be adopted, as done by Hagen and Rosetti. And if the number of the terms of the expression be great, then it loses that simplicity which alone fulfils the requirements we have a right to claim in a natural expression for the phenomena of nature. In addition to this, Hagen expressed the variation of specific gravity by a formula of the aspect

$$S_t = 1 - (t-t_m)^2 [A - B(t-t_m)^{1.6}]^2,$$

while Rosetti had recourse to a similar formula for the expression of the volumes:

$$V_t = 1 + A(t-t_m)^2 - B(t-t_m)^{2.6} + C(t-t_m)^{3.2},$$

and since  $V_t S_t = 1$ , a comparison of both expressions, as well as a trial of them, convinces one of the total unsatisfactoriness of both or at least one of them.

numerous calculations that  $F(t)$  is expressed by the sum of the terms  $a + bt + ct^2 + dt^3 + \dots$  with coefficients consecutively changing their signs, *i. e.* from + to -, and decreasing in magnitude\*. This indicated the convergent nature of the series and the possibility of expressing  $F(t)$  in a simpler form which would rapidly converge. But I did not consider it as sufficiently exact, for the admission of terms with  $t^2$  and even  $t^4$  in  $F(t)$  did not yet express the entire phenomenon of the expansion of water between  $-10^\circ$  and  $+200^\circ$  with even the small degree of accuracy which is found in contemporary determinations. In striving to express  $F(t)$  in the simplest possible form I tried many of the expressions already proposed, but became convinced of their insufficiency†. As regards formula No. 1, I arrived at it from the following considerations:—

1. When I showed (see note p. 101) that the expansion of all liquids (except water) may be approximately expressed, like the expansion of gases, by the general formula

$$V_t = \left(1 + \frac{kt}{n}\right)^n,$$

where for gases  $n = +1$  and for liquids  $n = -1$ , *i. e.* when for liquids it was possible to take

$$S_t = S_0 (1 - kt). \quad \dots \quad (3)$$

\* As an example I will cite one such formula, performing the multiplication by  $(t-4)^3$  in order to show clearly the varying nature of the signs:

$$S_t 10^6 = 999875 + 63.606 t - 8.3185 t^2 + 0.063238 t^3 \\ - 0.00036703 t^4 + 0.000006979 t^5.$$

Expressions with  $-At^2 + Bt^3$  can be considered as sufficient for the accuracy of contemporary determinations, but the above expression with  $t^5$ , although satisfying the greater portion of the curve, still, for ordinary temperatures ( $20^\circ$ – $30^\circ$ ) affords deviations which exceed the probable errors in corrected mean values.

† I for a long time confined my attention particularly to expressions of the form

$$\sqrt[3]{\frac{1}{S_t}} = 1 + (t-4)^3 F_1(t),$$

where the first member corresponds to the distance between the centres of the particles. I afterwards endeavoured to express the dependence of the density and of the volume of water upon its temperature by taking fractional indices (like Hagen and Rosetti) and tried the application of logarithmic (like Rankine) and catenary functions, and in general, like Hagen and Frankenheim, spent much time in endeavours to express this dependence by means of some simple algebraical formula with the least possible number of constants.

Then Thorpe and Rücker \* concluded, on the bases of Van der Waals's theory, that the modulus of expansion of liquids  $k$  stands in intimate dependence on the temperature of their absolute boiling-points  $T_2$ , namely that

$$\frac{1}{k} = 2T_2 - 273. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As in formula No. 2,  $F(t)$  is essentially analogous in its signification to  $k$  in formula No. 3, I tried to calculate the value of  $\frac{1}{F(t)}$  or  $\phi(t)$  instead of  $F(t)$ , hoping thus to include the conception of the absolute boiling-point of water, and this led to the form of formula No. 1.

2. It was necessary for the complete expression of the expansion of water as a liquid that  $F(t)$  should remain a positive fraction less than unity at all values of  $t$ , starting from a certain "critical" low temperature (below  $-10^\circ$ ),  $T_1$ , at which water solidifies under any condition (of pressure, electrical state, &c.), up to the higher "critical" temperature or absolute boiling-point  $T_2$ , at which water passes into vapour under any condition; because it is only between these two limits  $T_2$  and  $T_1$  that the specific gravity of liquid water can be observed. Outside these limits  $F(t)$  may acquire an imaginary value, or become greater than unity, or negative in sign. The form of formula No. 1 answers to these requirements for  $F(t)$ , because according to it

$$F(t) = \frac{1}{(A+t)(B-t)C} = \frac{1}{\phi(t)}.$$

3. It is known that if certain conditions be observed water may be cooled to  $-10^\circ$ , and even much lower, without being converted into ice, and therefore  $A$  must be greater than 10. On the other hand, Dewar † showed that the absolute boiling-point of water does not lie below  $+370^\circ$ , therefore  $B$  must be greater than 370; and as  $2T_2$  enters into formula No. 4, we may suppose that  $B$  will express a quantity greater than  $2T_2$ , and that the value of it will be greater than  $2T_1$ .

4. These considerations of a theoretical character led me to conclude that the value of  $\phi(t)$  should be found for various temperatures, and if these considerations were correct, that  $(t-4)^2/(1-S_2)$  or  $\phi(t)$  should be expressible by the parabola

$$\phi(t) = a + bt + ct^2,$$

\* Thorpe and Rücker, *Journal of the Chem. Soc.*, April 1884, xlv. p. 135.

† Dewar, *Phil. Mag.* 1884, (5) xviii. p. 210.

where  $a$  and  $b$  are positive and  $c$  negative; for then  $ABC=a$ ,  $(B-A)C=b$ , and  $-C=c$ , for

$$(A+t)(B-t)C=ABC+(B-A)Ct-Ct^2.$$

Besides, under the above conditions  $1/\phi(t)$  or  $F(t)$  should expand in terms of  $t$  into a convergent series with changing signs, as is obtained in reality.

By taking from the most trustworthy determinations the values of  $\phi(t)$  corrected as far as possible for temperatures  $20^\circ$ ,  $30^\circ$ ,  $40^\circ$ ,  $50^\circ$ ,  $60^\circ$ ,  $70^\circ$ , and  $80^\circ$ , and employing the method of least squares \*, I obtained:—

$$\phi(t)=125780+1158t-1.90t^2, \quad . \quad . \quad . \quad (5)$$

and the mean quadratic error of calculation proved to be far less than the possible error of experimental results. As a final verification of the formula obtained, the values of  $S_t$  were extrapolated by means of the expression No. 5 throughout the range of temperatures from  $-10^\circ$  to  $200^\circ$ , and it was found that the difference between the values obtained by experiment and calculation in no case exceeded the errors which must be recognized as existing in the determinations of the density of water. The figures thus obtained are given in Table III.

5. As the extrapolation was extended beyond the range of my calculations (from  $20^\circ$  to  $80^\circ$ , =  $60^\circ$ ) up to limiting temperatures exceeding more than three times the one adopted (from  $-10^\circ$  to  $200^\circ$ , =  $210^\circ$ ), and as formula No. 1 justified itself by a possible concordance with experimental results, and since the accuracy of existent determinations is very dissimilar and generally speaking small, I considered it useless, pending the publication of more accurate determinations, to search for a more trustworthy value of  $\phi(t)$  or through it of the value of  $S$ , taking the aggregate of all contemporary data; and this all the more, seeing that for ordinary temperatures (from  $0^\circ$  to  $40^\circ$ ) the values  $\phi(t)$  and  $S$  found from formula No. 5 were entirely satisfactory. Taking into consideration the fact that in the expression

$$y=a+bt+ct^2$$

the values of the parabolic coefficients,  $a$ ,  $b$  and  $c$ , deduced from experimental data by the method of least squares, are greatly

\* In all my calculations, when it was necessary to adopt the method of least squares I used the process of computation based upon P. L. Tchebysheff's method, which is fully explained in my work upon "The Compounds of Alcohol and Water," 1865, p. 89.

affected \* by the existence of errors in the fundamental quantities, it appears useless at present to expect values of any accuracy for the constants A, B, and C in formula No. 1. According to the numbers of formula No. 5, we find that

$$A=94\cdot10, \quad B=703\cdot51, \quad C=1\cdot90. \quad . \quad . \quad . \quad (6)$$

These figures satisfy the conditions  $A > 10$  and  $B > 370$ , and also that they should be all positive and greater than unity, so that  $F(t) > 0$  and  $< 1$ ; but the true values of A, B, and C can only be found after fresh and more accurate determinations. As a first approximation, especially for ordinary temperatures †, the above values will suffice, justified as they are by a comparison of the calculated results with the aggregate of already known data (see Tables I., II., III.).

Previous to revising the extant information concerning the expansion of water, it will be well to examine the corrections and errors relating to the data of the subject. On this head special attention must be paid to the influence of pressure, the coefficients of expansion of solid bodies, and the methods employed for determining the temperatures.

*Influence of Pressure.*—Taking the aggregate of results from previous sources (Regnault, Wertheim, Grassi, Amaury, and others) of information about the compressibility of water, it appears that the magnitude  $\mu$  (the coefficient of compressibility corresponding to a rise of pressure equal to one atmosphere) decreases when the temperature rises from  $0^\circ$ , whereas for all other liquids  $\mu$  increases with the temperature. The researches of Pagliani and Vicentini ‡, however, show that

\* In Prof. Markoff's researches (Proceedings of the Imp. Acad. of Sciences, St. Petersburg, 1889), the possible variations of  $a$ ,  $b$ , &  $c$  in the expression  $y=a+bx+cx^2$  for a given limit of the variable  $x$  and a determinate error of the variable  $y$  are considered in an exhaustive manner. This question is stated and solved for a particular case in the work "Investigation of Aqueous Solutions according to their Specific Gravity," 1887, p. 289, by the present Author.

† If we had to deal with a small range of temperature, for instance from  $0^\circ$ – $40^\circ$ , then the rectilinear expression of  $\phi(t)$  would amply suffice within the limits of possible errors (see Tables II. and III.). In that case

$$S_t = 1 - \frac{(t-4)^2}{A+B}.$$

A like expression, with the difference that in the numerator  $(t-4)$  has an index of more than 2 and less than 3, appears sufficient for the entire range of expansion, but then great difficulty is experienced in the calculations and in reality three constants are introduced, the same as in formula No. 1. But an expression of the form

$$S_t = 1 - \frac{(t-4)^2}{A+Bt},$$

proves unsatisfactory.

‡ Pagliani and Vicentini. Unfortunately I have not read their memoir in the original, but only know it from an account published in Wiedemann's *Beiblätter*, 1884.

## Density of Water with the Temperature

this decrease only extends to a temperature approach and that beyond, for water as for other liquids, viz. :—

	By experiment.	By formula
0°.	$\mu 10^6 = 50\cdot3$	$\mu_t 10^6 = 50$
10°.	47·0	47
20°.	44·5	44
30°.	42·5	42
40°.	40·9	40
50°.	39·7	39
60°.	38·9	38
70°.	39·0	39
80°.	39·6	39
90°.	40·2	40
100°.	41·0	41

In order to be able to deal with experimental temperatures exceeding 100°, I have expressed the  $\mu$  by a parabola :—

$$\mu = 10^{-6}(50\cdot49 - 0\cdot348 t + 0\cdot0026 t^2).$$

Since the quantity  $\mu$  represents some hundredth of the volume, it is evident that in determining  $\mu$  for water (just the same as for all other liquids) it is to obtain results agreeing to a millionth, even at atmospheric pressures, if (as is usually done) we neglect influences of compressibility and pressure. So, for example, that the experimenter had determined  $\mu$  for water at 100° as 1·043212, operating at a pressure of one atmosphere; and on another occasion with this pressure by one tenth of an atmosphere, he ought to find 1·0000042 or 1·043216, if his determinations are accurate to a millionth. The influence of compressibility is particularly notable when determining the density of water beyond 100°, because at such temperatures the influences are unavoidably considerable. In this respect the experimental, reconnoitring determinations were made

\* Sorby (Phil. Mag. 1859, xviii. p. 81) made his determinations in a cylindrical sealed tube, and compared the volumes of water and saline solutions. His data refer to vapour-pressures  $p$  at the temperature indicated.

$t = 120^\circ$	$140^\circ$	$160^\circ$	$180^\circ$	$200^\circ$
$p = 1\cdot98$	3·57	6·12	9·93	15
$V = 1\cdot05988$	1·0796	1·10186	1·12676	1

Judging from the mode of observation, the degree of expansion exceeds  $\pm 0\cdot005$ .

In 1860, being unaware of Sorby's determinations, I made determinations of the expansion, above their boiling-point, of ether, and alcohol (Mendeléeff, Liebig's *Ann.* cxix. p. 1). I

and myself, and showed that beyond  $100^{\circ}$  the expansion of water increases just the same as at lower temperatures. Later on Hirn \* accurately determined the variation of a volume of water heated from  $100^{\circ}$  to  $200^{\circ}$ , allowing it to remain all the time under a pressure of about 15 atmospheres. Taking the volume at  $4^{\circ}$  to be unity and taking, according to Despretz,  $V_t = 1.04315$  for  $100^{\circ}$ , it appeared that, for

$120^{\circ}$	$140^{\circ}$	$160^{\circ}$	$180^{\circ}$	$200^{\circ}$
$V_t = 1.05992$	$1.07949$	$1.10149$	$1.12678$	$1.15777$

In order to render these figures comparable with the other data for a pressure of one atmosphere, it is necessary to multiply them by  $(1 + \mu_t 14)$ , since the volumes were observed under a pressure of 15 atmospheres †. This reduction necessitates the knowledge of  $\mu_t$  between  $100^{\circ}$  and  $200^{\circ}$  inclusive. Up to the present time direct determinations of this kind do not exist, so that it becomes necessary to extrapolate by means of formula No. 7. This gives for the above temperatures :—

$$10^6 \mu_t = 46.17, \quad 52.73, \quad 61.37, \quad 73.09, \quad 84.89.$$

Therefore Hirn's figures for the volumes of water when reduced to a pressure of one atmosphere become :—

$$V_t = 1.06060, \quad 1.08029, \quad 1.10244, \quad 1.12793, \quad 1.15914.$$

Determining from these the density under a pressure of one atmosphere, we have

$$S_t = 0.94286, \quad 0.92568, \quad 0.90708, \quad 0.88658, \quad 0.86271.$$

like Sorby's, were only intended to give a preliminary acquaintance with the phenomenon, and my error is still greater than Sorby's, namely about  $\pm 0.01$ . For water a determination was made for three temperatures, and gave the following results :—

$t = 120^{\circ}$	$140^{\circ}$	$160^{\circ}$
$V = 1.07$	$1.09$	$1.11$

The volumes were reduced to a pressure of 1 atm. Sorby's and my results are incomparably less accurate than those made by Hirn, and as such have not met with any further attention. This was a first reconnaissance into the region of the unknown.

\* Hirn, 1867, *Ann. de Chimie et Phys.* (4) x. p. 32. The method of determination and the dimensions of the vessels adopted guarantee considerable accuracy to Hirn's results, which, however, judging from the mode of computing the corrections, especially for the coefficient of expansion of the vessel, contain an error hardly less than  $\pm 0.0005$ .

† Hirn states in his memoir (*l. c.*) on p. 39, that the height of the mercury in the open column was 11.25 metres; but on p. 48 he says that the mean pressure was equal to 11.5 metres. Taking the first statement and adding the atmospheric pressure, we obtain 15.8 atm., but if we take the height 11.5 metres to express the total pressure we obtain 15.1 atm.



However well the results of Hirn's repeated experiments may agree with one another, still they must contain errors which it is impossible to avoid, but which should not be lost sight of. Thus, for instance, Hirn determined the expansion of his copper vessel between  $22^{\circ}$  and  $101.78^{\circ}$ , using water and the figures representing its variation in volume given by Despretz (Table I.). We know that these results, although derived from one of the best determinations, are somewhat in error, especially at about  $20^{\circ}$  (Table I.), and therefore, on their basis, the true coefficient of expansion of the copper vessel cannot be obtained \*. According to Hirn 0.00005024 was determined to be the coefficient of cubical expansion, and this value was adopted in his calculation. But Fizeau gives for copper 0.00005034 at  $40^{\circ}$  and 0.00005094 at  $50^{\circ}$ , showing a rapid increase with the temperature. This also follows from the determinations of Dulong and Petit, who demonstrated that the linear expansion from  $0^{\circ}$  to  $100^{\circ}$  is 0.00001718 and 0.00001883 from  $0^{\circ}$  to  $300^{\circ}$ ; whence it may be supposed that if the mean coefficient of cubical expansion of copper from  $0^{\circ}$  to  $100^{\circ}$  is 0.000051, then from  $100^{\circ}$  to  $200^{\circ}$  it will be 0.000056. In general the coefficient of expansion of copper increases with the temperature. Hirn took this quantity as constant, and thus introduced an error amounting to 0.000005, which in temperatures ranging from  $100^{\circ}$  to  $200^{\circ}$  involves an error of not less than 0.0005 in the volumes of water. Since, then, the reduction from 15 atmospheres to 1 atmosphere was made by us on the basis of extrapolation, and very probably the true compressibility of water between  $100^{\circ}$  and  $200^{\circ}$  is

\* Water, however, is the most convenient liquid for determining the coefficient of expansion of vessels; and if the data for the expansion of water be complete we may prefer it to all other liquids, especially for the determination of the expansion of glass vessels at moderate temperatures, because in this case water varies in volume very slightly. The following simple method, which I have practised for a long time, gives very rapid and concordant results for the coefficient of expansion of glass at temperatures near  $0^{\circ}$ . The vessel is filled with water at  $0^{\circ}$ , up to a mark, and then carefully heated; at first the level falls, but then at a certain temperature  $t$  it again returns to the former level. The determination of  $t$  gives  $k$ . Evidently the volume of the vessel at  $0^{\circ}$  and at  $t$  is equal to the volume of water  $V_0$  and  $V_t$  at these temperatures; and hence the ratio

$$\frac{V}{V_0} = 1 + kt.$$

In this manner the expansion of vessels can be rapidly determined by means of a corrected thermometer, and the relative results obtained are very precise. This method may be of especial use in the study of areometers.

much greater than that adopted by us \*, and since this reduction affected the third decimal in the volumes, it may be presumed that the above-determined densities of water contain an error at least in the fourth, or perhaps even in the third decimal place.

Having made this reservation, it will be possible to compare the densities found by experiment with those calculated from formula No. 1, adopting the above-mentioned values for the constants A, B, and C. Thus:—

	120°.	140°.	160°.	180°.	200°.
From Hirn's experiments, $S_t =$	0.9429	0.9257	0.9071	0.8886	0.8627
By calculation, formula No. 1 =	0.9433	0.9262	0.9073	0.8864	0.8635
Difference .....	-0.0004	-0.0005	-0.0002	+0.0002	-0.0008

The difference, therefore, between the results obtained by experiment and by calculation, for temperatures ranging from 100° to 200°, does not exceed the possible error in the determinations made by Hirn, which are distinguished by the highest degree of accuracy yet attained in this province.

With respect to the influence of pressure on the density of water, we must, *inter alia*, make the following remarks:—

(1) A most important addition to the study of the properties of water will be introduced by determining with the greatest possible accuracy its compressibility between  $-10^\circ$  and  $+200^\circ$ .

(2) In accurate determinations of the density of water (and of other liquids) the pressure must be determined and a correction introduced for it.

(3) The normal density of liquids (also of gases) must be reckoned at the normal pressure of 760 mm. of mercury (at lat. =  $45^\circ$ ).

(4) For the theory of the subject it would be highly important to make a series of determinations of the density of water from  $0^\circ$  to  $100^\circ$  and upwards at some fixed and considerable pressure, in order to judge of the manner in which  $S$  and  $V$  are dependent on  $t$  and  $p$  (pressure). At present, whilst we are ignorant of the true nature of this dependence, we may take

$$S_{t,p} = \left[ 1 - \frac{(t-4)^2}{\phi(t)} \right] \left[ 1 + \mu_t(p-1) \right],$$

if  $\phi(t)$  be found for  $p=1$  atmosphere. From the theory of

\* Pagliani showed that with the majority of investigated liquids  $\mu$  increases very rapidly with the temperature; for instance, with normal propyl alcohol, at  $0^\circ$ ,  $\mu=0.0000086$ , and at  $100^\circ$   $\mu=0.0000158$ . Judging from the variation of the properties of water, there is reason for thinking that at  $200^\circ$  its coefficient of compressibility will be, for example, twice as great as at  $100^\circ$ .

heat (Thomson, Van der Waals, Tait, and others) we know of the existence of a sort of relation between the pressure and melting-points of ice and the maximum density of water; also that with respect to this last property Amagat demonstrated a lowering of the temperature of the maximum density as the pressure rises\*; but the fact of a change of density being dependent upon an alteration of pressure at different temperatures, although theoretically admissible, still requires experimental investigations, confirming those general laws which govern the volumes of gases and liquids in relation to changes of temperature and pressure.

*The Influence of the Expansion of Solids.*—For water as yet we have no determinations of expansion made independently of a change of volume in other bodies (for instance, the containing vessel or solids in general), because the process of determining the height of columns of water at different temperatures presents practical difficulties which I consider it out of place to take into account here, but which I desire to overcome if it be at all possible. The true volume of water,  $V_t$ , is determined from the apparent (observed) volume  $W_t$  by multiplying it† by the changed volume  $v_t$  of the solid envelope; hence it is evident that however accurate the measuring of the apparent volume be, the resulting  $V_t$  will include the entire error contained in the expansion of the envelope. As regards the expansion of envelopes, in spite of numerous investigations, there is a great deal of confusion and doubt and more or less improper application.

1. Very frequently‡, in order to obtain the true volume  $V_t$ ,

\* By using formula No. 7, it is easily seen that, as the pressure rises, the temperature of the maximum density falls, and that, at a pressure of 1000 atm., it will be far below  $+4^\circ$ . Hence it is necessary to consider the pressure when treating of questions relating to the temperature of the maximum density of water. I may here remark that the solution in water of alcohol, sulphuric acid, salt, &c., also lowers the temperature of the maximum density (and also that of the formation of ice); that is, it acts the same as compression.

† Regnault (*Relation des expér.* i. p. 225) remarked long ago that the addition of the apparent volume to the increase of volume of the vessels involves an incidental error, because the true expansion is equal to the apparent multiplied by the volume of the vessel.

‡ As an example I may cite the determinations of Weidner (*Pogg. Ann.* 1860, lxxix. p. 300). He was, however, fully justified in having recourse to a simplified method for determining the true volume of water, because his determinations were made at temperatures not differing from  $0^\circ$  by more than  $10^\circ$ , and were not distinguished for any great degree of accuracy. When the temperatures, on the other hand, lie distant from  $0^\circ$  and the precision of the investigation is considerable, then the usual method of finding the true volume from the apparent volume must be abandoned, as it is erroneous in principle and introduces errors which may easily be avoided.

the increment of the volume of the vessel, *i. e.*  $kt$ , is added to the apparent volume  $W_t$ , whereas  $V_t$  should be found from the product  $W_t \times v_t$ , where  $v_t = 1 + kt$ . An example will show how great an error is thus introduced. Supposing  $V_0 = 1$ , and let us assume the apparent volume of the water at  $100^\circ$  equal to  $1.040502$ , and let the coefficient of expansion of glass  $= 0.00002705$ . According to the generally adopted method, we should conclude from this that the true volume of water at  $100^\circ = 1.040502 + 0.002705 = 1.043207$ ; whereas in reality it is equal to  $1.040502 \times 1.002705 = 1.043316$ : thus the error committed  $= 0.000109$ , exceeding that of observations made in the simplest manner. Even with a difference of temperature from  $0^\circ$  not greater than  $20^\circ$ , the error of the above *modus operandi* is already clearly sensible in the sixth place. This error decreases, but does not disappear, when a similar method is employed in determining the coefficient of expansion of the vessel, *viz.* the subtraction of the apparent expansion of mercury from the true expansion.

2. The coefficient of expansion of glass and metals adopted when determining the density of water is usually taken for a range of temperature from  $0^\circ$  to  $100^\circ$ , and the mean value of the coefficient of expansion  $k$  of the envelope being found, it is taken as constant throughout the whole of this range. It is, however, beyond doubt, in spite of statements to the contrary\*, that the coefficient of expansion of glass increases considerably (relatively more than mercury) with the temperature. Hence the readings of the mercury thermometer, on being reduced to the normal hydrogen thermometer, require a negative correction and not a positive one, as would be necessary if the variations depended upon the unequal expansion of mercury alone†. From Regnault's

\* Hagen (*Abhandl. d. K. Akademie zu Berlin*, 1855, Math. i.), in a special examination of this question and taking as basis his determinations of the linear expansion of glass, states that, between  $0^\circ$  and  $100^\circ$ , the coefficient of cubical expansion of glass is without variation. Volkmann (*Wiedemann's Ann.* 1881, xiv. p. 270), in revising the determinations of Rosetti, who found  $k$  to increase with  $t$ , concludes by denying this variability, *i. e.* he considers  $k$  constant from  $0^\circ$  to  $100^\circ$ , as generally admitted by experimenters. I may here remark that in the investigation of other liquids, which have a large coefficient of expansion and offer but slight variations in it, this supposition does not play an essential part. But in water at low temperatures, the coefficient of expansion is small—for instance, between  $5^\circ$  and  $10^\circ$  it is equal to  $0.0000508$ , *i. e.* only twice that of glass; so that in this case the determination of small variations in the coefficient of expansion of glass is of great importance for the accuracy of the final result.

† Let  $t$  be the true temperature (according to the hydrogen thermometer), and let us suppose, without greatly departing from the truth in the abstract, that the expansion of mercury from  $0^\circ$  to  $100^\circ$  is expressed by

$$V_t = 1 + 0.000180t + 0.00000002t^2,$$

data we may deduce that ordinary glass between  $0^{\circ}$  and  $300^{\circ}$  undergoes a change of volume indicated by the equation

and the linear expansion of glass by

$$v_t = 1 + 0.000027 t.$$

The apparent expansion of mercury, as observed in the glass thermometer, will be  $\frac{V_t}{v_t}$ , and at  $100^{\circ}$  it will equal 1.015459. Every degree of

the mercury thermometer will correspond to a volume of 0.00015459, and  $50^{\circ}$  of the mercury thermometer will answer to an apparent volume of 1.0077295. The question then arises, What will be the true temperature  $t$ , above or below  $50^{\circ}$ ? When  $t = 50^{\circ}$ , the apparent volume equals  $\frac{1.009050}{1.001350} = 1.0076896$ : hence the difference between this volume and that at which the mercury thermometer shows  $50^{\circ}$  is equal to 0.0000399, corresponding to  $0^{\circ}.258$  nearly. Therefore, if the variation of the volume of the glass were expressed lineally (*i. e.* if the coefficient of expansion of glass were constant), then, when the mercury thermometer showed  $50^{\circ}$ , the true temperature would be  $50^{\circ}.258$  and the correction for the readings of the mercury thermometer would be positive. This correction would remain positive so long as the variation in the coefficient of expansion of glass were less than that of mercury; for which latter the value of  $b$  in the parabola  $V = 1 + at + bt^2$  is 9000 times less than  $a$ . But when this relation grows greater for glass, then the correction will become negative. Let us illustrate this by an example, taking the same expansion for mercury as above, and for glass

$$v_t = 1 + 0.000025 t + 0.0000002 t^2;$$

*i. e.* let us suppose that its coefficient of expansion changes more rapidly with the temperature than mercury. The apparent expansion of mercury up to  $100^{\circ}$  will be as before, since the volume of the envelope will be 1.0027 at  $100^{\circ}$ ; therefore one degree will again correspond to 0.0001546 of the volume and a reading of  $50^{\circ}$  on the mercury thermometer will be obtained, when the apparent volume equals 1.0077295. But at the true, temperature  $t = 50^{\circ}$ , the apparent volume will be  $\frac{1.009050}{1.001300} = 1.0077391$ .

Hence when the mercury thermometer shows  $50^{\circ}$ , then the true temperature will be  $49^{\circ}.938$ , and the correction for the readings of the mercury thermometer at  $50^{\circ}$  will then be negative. All the investigations which have been made on the corrections for mercury thermometers by comparing them with the hydrogen thermometer, show (as mentioned in a subsequent note) that the correction for readings, verified in every other respect, of mercury thermometers is negative; *i. e.* the true temperature is lower than that shown by a mercury thermometer which has been corrected for zero, calibre, &c. throughout the entire range from  $0^{\circ}$  to  $100^{\circ}$ . Hence it is clear that (1) the variation of the volume of glass does not proceed according to a linear function of the temperature, which is the same in the case of the expansion of mercury (the latter follows from Regnault's determinations of the true expansion of mercury); and (2) the coefficient of expansion of glass increases relatively more rapidly than that of mercury.

I thought it well to demonstrate the last two propositions for three reasons:—(1) I have nowhere met with a simple, objective treatment of this subject; (2) generally the proportionality of the expansion of glass to the temperature is adopted without further discussion, or else the absence of this proportionality is considered as not proved, Hagen, Matthiessen, and others being cited; and (3) in the question of the expansion of water, true data for the expansion of glass are of very great importance.

$$v_t = 1 + (25.3 + 0.0062 t) 10^{-6} t.$$

Now the true expansion of mercury through the same range of  $t$  is expressed by the formula

$$V_t = 1 + (179.97 + 0.0208 t) 10^{-6} t.$$

Thus the coefficient of cubical expansion of glass is seven times less than that of mercury, while its thermal increment is only three times less. The conclusion arrived at by Benoit\* is still more convincing. He found that between  $0^\circ$  and  $40^\circ$  the variation in volume of ordinary glass is expressed by

$$v_t = 1 + (21.552 + 0.0241 t) 10^{-6} t;$$

while, according to Broch, the expansion of mercury through this range of temperature is

$$V_t = 1 + (181.652 + 0.004845 t) 10^{-6} t.$$

Here the increment of the coefficient of expansion of glass is absolutely greater than that of mercury, although at  $0^\circ$  the coefficient itself is more than  $7\frac{1}{2}$  times less. From this it is evident that by taking the coefficient of expansion of glass as constant, an error is introduced which affects the result very palpably. Thus, for instance, if the true expansion of glass between  $0^\circ$  and  $100^\circ$  be expressed by the parabola

$$\frac{v_t}{v_0} = 1 + (25 + 0.02 t) 10^{-6} t,$$

then the volume at  $100^\circ$  will be 1.0027 and the mean coefficient of expansion will equal 0.000027; whence it may be supposed, for instance, that at  $20^\circ$  the volume of the vessel should be 1.000540, whereas in reality it is 1.000508, giving a difference

\* Deductions from the observations of Benoit and Broch, taken from the work by Guillaume, *Traité pratique de la thermométrie de précision*, 1889, p. 336, which forms one of the fruits of the labours of the International Bureau of Weights and Measures. As regards the above-cited consequence of Regnault's determinations (*Relation des expér. t. i. p. 225*), I calculated as follows:—From observation, it appeared that the apparent expansion of mercury is expressed by the equation

$$W_t = 1 + (154.28 + 0.00987 t) 10^{-6} t;$$

and from determinations of the true expansion of mercury, I had previously calculated (Journal of the Russian Physico-Chemical Soc., Physical Section, 1875, p. 75) that it is expressed, for the same limits of temperature, in the manner given in the text, and hence the expression given above for the volumes of glass. From these data it would have been possible to deduce the variation of the coefficient of expansion of glass, if experiment had not shown that the amount of this variation is very dissimilar for different kinds of glass.

(0.000032) in the volumes which exceeds the possible errors of reading (gravimetric or volumetric). Still up to now our information respecting the variation in the coefficient of expansion of vessels with rise of temperature is not sufficiently clear to allow of its employment as the means of introducing into the existing data respecting the expansion of water corrections which would really improve our results. At present we can only say that, in determining the volume of a vessel according to the formula  $v_t = v_0(1 + kt)$ , and finding  $k$  for a change of  $t$  from  $0^\circ$  to  $100^\circ$ , the greatest errors are introduced between  $25^\circ$  and  $75^\circ$  and that they attain some hundred-thousandths of the volume or of the density.

3. Many observers (Hallström, Stampfer, Hagen, Matthiessen) determined the expansion of the solids adopted in the hydrostatic determination of the variation of the density of water, by measuring the linear expansion of the substance from which the body weighed in water was prepared. This method, which does not require a knowledge of the expansion of mercury, involves, firstly, three times the error accompanying the determination of the linear expansion, which error, notwithstanding all the improved methods of determination, is still sufficiently great and will scarcely give a result with an approximation of more than hundredths; secondly, it is presumed, *à priori*, that the expansion in a transverse direction is the same as longitudinally, even for drawn-glass tubes, which fact needs demonstration, and in my opinion is very unlikely; and, thirdly, the above-mentioned method is most often applied to glass tubes from which the body used in hydrostatic weighing is made by blowing or melting; and it is likely that such deformation involves some change in the coefficient of expansion. In addition to this Hallström (1825) found that the cubical expansion of glass is greatly affected by a rise of temperature:

$$v_t = 1 + (5.88 + 0.315t)10^{-6}t;$$

whereas Hagen (in 1855) found hardly any variation in the coefficient of expansion in the glass he used (through a range of  $1.6^\circ$ – $81^\circ$ ), and gave the value:

$$v_t = 1 + 27.69t10^{-6}.$$

According to the first formula, the volume at  $70^\circ = 1.001955$ , and from the second we obtain  $1.001938$ —results nearly the same; but at other temperatures these values vary considerably, for instance at  $30^\circ$  the first formula gives  $V = 1.000460$ , against  $1.000831$  according to the second.

Neither of these contradictory results can be considered as correct or depending only on the properties of glass, and

probably the conflicting evidence of the observers has its source in the errors accompanying the determination of the linear expansion of solids by the method of comparison.

4. No less doubtful are the determinations of the expansion of glass, carried out between  $0^{\circ}$  and  $100^{\circ}$ , by means of mercury, because the true *mean* coefficient of expansion of mercury adopted by different observers varies greatly, and it is impossible to say at present to what extent the actual value differs from those taken\*. After the determinations of Dulong and Petit, this mean coefficient of expansion of mercury was taken as  $\frac{1}{5550} = 0.00018018$ ; Regnault deduced the value  $0.00018153$  from his classical researches. By applying different methods of interpolation to the determinations of Regnault (expressing the result multiplied by  $10^6$ ), Bosscha (1874) found 18241; Galton (1873), 18181; Wüllner (1874), 18252; Mendeléeff (1875),  $18210 \pm 7$  †; Levy (1881), 18207; and Broch (1885), 18216. The chief cause of this discrepancy in the results lies in the circumstance that Regnault, out of 135 determinations, only made 32 for temperatures below  $100^{\circ}$ ; his cold column of mercury during the experiments was not at  $0^{\circ}$ , but had a temperature from  $+10$  to  $+18^{\circ}$ , and separate experiments present differences amounting to the discrepancies above stated. Without fresh

\* The method pursued up to now since the time of Dulong consists in determining the true expansion of mercury, then from it that of glass, and, knowing the latter, from the apparent expansion the true expansion of water and of other liquids. The great difference (7-fold) between the coefficients of expansion of glass and mercury constitutes the weak point of this method, because the expansion of mercury must be ascertained with a degree of precision scarcely attainable in experiments. But the most perceptible want in this method lies in the fact that the classical researches of Regnault afford very little material for an accurate judgment of the expansion of mercury between  $0^{\circ}$  and  $100^{\circ}$ , where questions of expansion are mainly concentrated and where observations are most within reach. The great necessity for new determinations of the true expansion of mercury from  $0^{\circ}$  to  $100^{\circ}$  has already repeatedly been made manifest. I unite my voice to that of many others; but I will add that when we have reliable figures expressing the expansion of water it will then be easier to obtain them for mercury also, for experiments with water, between  $0^{\circ}$  and  $100^{\circ}$ , are easier and more convenient than with mercury, and consequently their precision may be greater. In a word, the determination of the true expansion of water is a question urgently requiring solution.

† I think it will not be superfluous here to draw attention to the fact that in the determinations of the expansion of mercury from  $0^{\circ}$  to  $100^{\circ}$  (according to Regnault) there, without doubt, exists an error, attaining  $\pm 7$  or 8 millionths of the volume; and therefore it is necessary to recognize this possible error in the calculations and to determine it, which I have endeavoured to do. The calculations of Levy and Broch, made subsequently to mine, justified my conclusion, since the difference between their result and mine does not exceed  $\pm 7$  millionths.



determinations this question will remain doubtful for the future within the limits I indicate ( $\pm 7$  for 18210). Matthiessen (1865) having determined the coefficient of expansion of glass and water, employed them for fresh determinations of the expansion of mercury, but his results are not sufficiently accurate to elucidate the matter \*. Besides this, as the mean coefficient of expansion of mercury from  $0^\circ$  to  $100^\circ$  does not give the variation of the coefficient of expansion of glass, which variation must be recognized, therefore we must allow an error, affecting the fifth decimal place, in the data for the volumes of water, which error proceeds entirely from the fact of taking the mean coefficient of mercury as a basis.

*The Determination of Temperatures.*—The majority of the determinations of the variation of the density of water with a rise of temperature have been made with the aid of ordinary mercury thermometers, correcting their readings relative to the position of zero and to calibration, although to the exclusion of all that sum of corrections, which the researches of Pernet, Guillaume, and other observers in the Metrical Committee † have recently elucidated. Jolly (1864), however, in his determinations, referred the temperatures to the air thermometer directly. In searching, however, for the true law of the expansion of water, it is necessary to express the temperatures by the absolute scale or by the hydrogen thermometer, because in the law of the expansion of liquids we must expect a direct connexion with the law of the expansion of gases, since there is great similarity, although no identity, between the liquid and gaseous states of matter. In order to show how great is the influence of the circumstance alluded to above, we give the values, from Chappuis' experiments, of the correction  $\Delta t$  which must be added to the readings of a mercury thermometer of hard glass (whose analysis is  $71.5\% \text{SiO}_2$ ,  $14.5\% \text{CaO}$ ,  $11\% \text{Na}_2\text{O}$ ,  $1.3\% \text{Al}_2\text{O}_3$ ) to convert them to the scale of the hydrogen thermometer :—

— $10^\circ$ .	$\Delta t = +0.073$ ;	$ds/dt = +0.000284$ ;	$\Delta S = -0.000019$
0°.	0	+0.000065	0
20°.	—0.085	—0.000148	—0.000013
40°.	—0.107	—0.000380	—0.000041
60°.	—0.090	—0.000512	—0.000046
80°.	—0.050	—0.000621	—0.000031
100°.	0	—0.000718	0

Along with the corrections  $\Delta t$  are given the values of the differential coefficient  $ds/dt$  or the variations in the density of

\* Matthiessen, Pogg. *Ann.* 1865, cxxviii. p. 512. † See note p. 114.

water, corresponding to one degree, and after are shown the corrections  $\Delta S$  for the specific gravity of water which must be introduced, in order to obtain from the observed quantities these specific gravities as referred to the hydrogen thermometer. Here also the corrections for the figures given by the experimenters apparently affect the fifth decimal. And since in the constancy of the temperatures and in the readings of the thermometers we must allow, besides, their own inevitable errors, and seeing that, in addition to this, these errors differ with different observers and thermometers\*, it may be considered as demonstrated that in general in the data existing at present for the density of water, at 20° for instance, not only the sixth but the fifth decimal place is subject to correction.

But what is the magnitude of possible error in perfected determinations of the density of water, if we reckon that insignificant and individual errors disappear on taking a mean result, and making the figures more uniform by the method of interpolating introduced by all observers in their experiments, by expressing them in the form of densities referred to degrees?

I have devoted much time to the consideration of the best answer to this question: having endeavoured to determine by an examination of the original investigations, the measure of the errors of each experimenter by introducing into his results all the possible corrections, and calculating the mean quadratic

\* Many investigators on the expansion of water at various temperatures have determined, if not all the possible error, at least the value of the deviations of the formulæ expressing the expansion from their experimental results. Thus, for instance, Hagen (*l. c.*) found for his observations, that the so-called "probable error," or more precisely the measure of the discrepancies between the experimental results and those given by formula, may be expressed in fractions of degrees of the temperature, which we translate into millionths of the volume.

From 0° to		In degrees.	In volumes.
	8°	$\pm 0.1033$	$\pm 0.000002$
" 8	" 14	0.1085	11
" 14	" 20	0.0479	8
" 20	" 30	0.0788	20
" 30	" 40	0.0439	14
" 40	" 60	0.0528	24
" 60	" 80	0.0592	36
" 80	" 100	0.1249	$\pm 0.0000086$

The greater portion of the errors of this kind (accidental) are eliminated in the majority of the investigations by the help of interpolation, by the method of least squares, and therefore in the sequence I avoid dwelling upon such errors, and pay chief attention to the constant errors in connexion with the fundamental methods of research, which cannot be removed by interpolation.

digressions of the interpolation-formulæ from the observed figures in various regions of temperature. But on comparing the results thus obtained, I have come to the conclusion that—1, the introduction of all the possible corrections does not make the results of separate observers agree with one another; and 2, the greatest quadratic deviations do not appear in the results of those observers whose results are apparently the least trustworthy, but in those cases where the methods adopted are described in the greatest detail and most circumstantially. For this reason, I give in Table I. the original figures of the observers without introducing any corrections whatever; and it is only to aid their comparison that I express the results in volumes, taking the volume at 4° equal to 10°. Further, in Table II. figures are given which have been determined at different times by various investigators, deduced from an aggregate of data corrected in all respects and considered as most trustworthy. Finally, in Tables II. and III., besides the densities and volumes of water found from formula No. 1, the magnitude of the errors, which may now be looked for in the best determinations, are given. These possible errors, inherent in contemporary data, may evidently also occur in the results given by formula No. 1, for its constants and very form could only be founded upon previous determinations.

Table I. contains the figures for the volumetric variations of water found by the following investigators:—

1. Hallström, in Abo (*Pogg. Ann.* i. p. 168). He made his determinations (in 1823) by weighing in water a glass sphere (vol. about 162 c. c.) blown out of the same material as a tube, whose linear expansion he determined in a direct manner. Hallström interpolated the specific gravities, taking that at 0° as unity, according to the formula

$$S_t = 1 + at - bt^2 + ct^3;$$

the constants, multiplied by 10°,  $a = 52.939$ ,  $b = 6.5322$ , and  $c = 0.01445$ , were found by the method of least squares for  $t$  from 0° to 30°. The determinations made by Hallström must be taken as exemplary. Subsequently Hagen and Matthiessen adopted the same method. The chief cause why the results obtained by Hallström are all below the truth, lies in the fact that his results for the linear expansion of glass, at temperatures between 0° and 30°, were below the actual figures. Taking  $k = 0.000026$ , we obtain results from Hallström's figures which very nearly approach the date of the best and latest determinations.

2. Muncke (*Mémoires prés. à l'Académie des Sciences de*

*St. Pétersbourg*, t. i. p. 249), in Heidelberg, made a determination of the expansion of numerous liquids by the volumetric or thermometric method, which was afterwards adopted by Despretz, Kopp, Pierre, and many others. Although Muncke's results were communicated to the Academy in 1828, they only appeared before the public in 1831, i. e. simultaneously with the investigations of Stampfer. Muncke determined the expansion of the vessel by means of mercury, taking the value given by Dulong and Petit ( $\frac{1}{5550}$ ). Muncke's results for low temperatures ( $0^{\circ}$  to  $30^{\circ}$ ) are greater than the actual values, and those for higher temperatures ( $40^{\circ}$  to  $100^{\circ}$ ) are less. This is due to the insufficient accuracy of calibration and to the determination of the coefficient of expansion of glass. It should be observed that most of the results of Muncke's researches appear inaccurate when compared with recent researches.

3. Stampfer (*Pogg. Ann.* xxi. p. 116) in 1831, in Vienna, determined the expansion of water hydrostatically by weighing a brass cylinder, whose linear expansion was previously determined and found to be 0.001920 between  $0^{\circ}$  and  $100^{\circ}$ . The determinations were conducted between  $-3^{\circ}$  and  $+40^{\circ}$ , and were expressed (taking the volume at  $4^{\circ}$  as unity) by the formula  $S_t = S_0 + at - bt^2 + ct^3 - dt^4$ . By the method of least squares the constants were:  $S_0 = 999887$ ,  $a = 60.932$ ,  $b = 8.4236$ ,  $c = 0.0580$ , and  $d = 0.0001207$ , on multiplying by  $10^6$ . Temperatures below zero appear for the first time in Stampfer's researches. For  $-3^{\circ}$  he gives the volume 1.000373; and since the difference of the volumes at  $-3^{\circ}$  and  $-5^{\circ}$  equals 0.000275, I have introduced the number 1.000648 for  $-5^{\circ}$ . The coefficient of expansion for brass given by Stampfer is too large, and hence the volumes exceed the true values.

4. Despretz (*Ann. de Chimie et de Phys.* t. 70. pp. 23, 47), in Paris, 1837. His determinations made at temperatures from  $-9^{\circ}$  to  $+15^{\circ}$  had chiefly in view the study of the densities near  $0^{\circ}$ . Despretz made but few determinations for temperatures from  $20^{\circ}$  to  $100^{\circ}$ , and only gave them to hundred-thousandths. But even these must be considered as among the most trustworthy up to the present date. The coefficient of expansion of glass was only determined for a portion of the dilatometers by means of mercury with Dulong and Petit's figures. From  $0^{\circ}$  to  $28^{\circ}$ , for glass,  $k = 0.0000255$ , and from  $0^{\circ}$  to  $100^{\circ}$   $k$  was equal to 0.0000258. For a long time Despretz's figures were in general use; and if they have been eventually replaced by more recent ones, such a change has not really any firm foundation. Generally speaking, our

information respecting the expansion of water from  $-10^{\circ}$  to  $100^{\circ}$  has hardly made any progress since Despretz's determinations, as regards their trustworthiness.

5. Pierre, in 1847, published a series of volumetric-thermometric determinations for the expansion of water, but did not calculate the ultimate figures. A complete calculation of Pierre's results from  $-10^{\circ}$  to  $100^{\circ}$  was subsequently made by Frankenheim (Pogg, *Ann.* 1852, lxxxvi. p. 463), whose figures are given in the table.

6. Kopp (Pogg. *Ann.* lxxii. p. 1), in 1874, like Pierre, measured the expansion of many definite liquids, and amongst them of water, chiefly with a view to compare the expansion of liquids up to their boiling-points. The method adopted was a volumetric-thermometric one. The coefficient of expansion of glass was deduced from mercury, taking Dulong and Petit's number. The calculations for the volumes are given in four separate equations for various ranges of temperature from  $0^{\circ}$  to  $100^{\circ}$ .

7. Plücker and Geissler (Pogg. *Ann.* 1852, lxxxvi. p. 238) adopted a method of compensation, and were the first to take Regnault's figures for the expansion of mercury. Into the thermometrical vessel, whose coefficient of expansion was determined by means of mercury between  $0^{\circ}$  and  $100^{\circ}$ , as much mercury was poured as was necessary to compensate the expansion of the vessel, and hence the quantity of water subsequently introduced was considered to expand in a space whose volume remained unaffected by a rise of temperature. In these determinations too much mercury was taken, so that the apparent expansion of the water contains a certain excess (as Miller observed in 1856); secondly, the mean coefficient of expansion of mercury between  $0^{\circ}$  and  $100^{\circ}$  was taken to be the same as between  $-5^{\circ}$  and  $+15^{\circ}$ , which is evidently inaccurate (the true expansion of mercury between  $-5^{\circ}$  and  $+15^{\circ}$  being still unknown, for Regnault's determinations start at higher temperatures); and thirdly, the coefficient of expansion of the envelope between  $-5^{\circ}$  and  $+15^{\circ}$  is presumed to be equal to the mean coefficient of expansion between  $0^{\circ}$  and  $100^{\circ}$ , which is also inadmissible. But apart from these points, which are common to the determinations of other observers, the results given by Plücker and Geissler are distinguished for their remarkable accuracy, which shows that the method adopted by them is capable of giving admirable results, were the data of the expansion of mercury and glass fully known. These investigators expressed the results of their determinations graphically by a very well-proportioned curve, although for only a small range of temperature not far distant from  $0^{\circ}$ .

8. Hagen (*Abhandlungen d. Akad. zu Berlin*, 1855, Math. Abth. p. 1), adopting a hydrostatic method, made *one* series of determinations of the expansion of water, which is remarkable for its completeness. As has been already mentioned, he employed his own determinations of the linear expansion of glass and expressed its cubic expansion by  $1 + 0.00002754 t$ , for the material he employed. Hagen evidently injured the accuracy of his results by taking the expansion of glass as constant, although he paid due attention to determining the temperatures and weights with the greatest possible precision. Hagen expressed his determination for  $t$ , from  $0^\circ$  to  $100^\circ$ , by a formula which may be represented thus :

$$S_t = 1 - T^2(A + BT^{1.6})^2 ;$$

here  $T = t - 3.87$ .  $A$  and  $B$  are two constants, and the index 1.6 (or the power of  $T$ ) was found by a series of attempts to express the entire phenomenon of the expansion of water from  $0^\circ$  to  $100^\circ$  in the simplest form. I may here mention that on applying this formula to the aggregate of the existing data, and by changing the values of  $A$  and  $B$ , I became convinced of the impossibility of its satisfying with sufficient accuracy the data already known respecting the expansion of water between  $-10^\circ$  and  $200^\circ$ . Moreover, it should be observed that Hagen himself considers his figures as being nearer the truth for the lower than for the higher values of  $t$ , which fact is proved by a comparison with the results given by formula No. 1.

9 & 10. Jolly and Henrici (*Sitzgsb. d. Akad. München*, 1864, i. p. 160), being desirous of verifying the existing data for the expansion of water at temperatures above  $30^\circ$ , made a series of determinations by a volumetric-thermometric method (Jolly), and by weighing a known volume of water (Henrici). The temperatures were determined by thermometers compared with the air thermometer, and the coefficient of expansion of glass by the true coefficient of expansion of mercury as given by Regnault. The number of observations made below  $30^\circ$  was limited. Differences occur in the separate determinations of both observers to the extent of several ten thousandths.

11. Matthiessen (*Journ. of the Chem. Soc.* 1865, *Pogg. Ann.* cxxviii. p. 512), by applying methods similar to those used by Hallström and Hagen, obtained results which differed considerably from theirs, which shows that hydrostatic weighing and especially the determination of the linear expansion of glass do not afford that degree of accuracy which is generally expected from them. Moreover, the results of

the different series of observations often present differences to the amounts of ten-thousandths.

12. Weidner (*Pogg. Ann.* 1866, cxxix. p. 300) applied the volumetric-thermometric method for the determination of the expansion of water between  $0^{\circ}$  and  $-10^{\circ}$ . He determined the coefficient of expansion of glass, by means of mercury, between  $0^{\circ}$  and  $90^{\circ}$  for vessels blown out of the same glass, and obtained very discordant results from two determinations, viz. 0.00002625 and 0.00002424. He only adopted the former, but this gave larger volumes than found by other observers, which is especially apparent at  $0^{\circ}$ .

13. Rosetti (*Pogg. Ann. Ergänzt. Band*, v. p. 265), in 1869, published a fresh series of determinations for the density of water, which were made by a combination of the volumetric and gravimetric methods. He determined the coefficient of expansion of glass according to Regnault's data, and found it to increase with a rise of temperature. His observations were expressed by a formula of the form :

$$V_t = 1 + a(t-4)^2 - b(t-4)^{2.6} + c(t-4)^3,$$

or else in a formula where the last term  $(t-4)$  is not raised to the cube, but to the 3.2 power. In its latter form, Rosetti's formula recalls that given by Hagen.

The figures given in Table I. are taken direct from the final results of the different observers, and without doubt contain some errors which in course of time will be capable of correction, so as to render the values for the volumes of water more accurate. Such corrections, or a revision of the mean of equally trustworthy determinations, have been undertaken more than once, and the results thus obtained are brought together in Table II. Although I consider it right to cite these results, and even myself proposed, in 1884, a similar revision for corrected averages, yet at the present moment, after having studied the subject more closely and recognizing the insufficiency of many of the corrections, I do not think it necessary to dwell especially upon this question, as, in the absence of new determinations, notably for the expansion of mercury and glass, it is impossible to hope to add to the trustworthiness of what is already known.

In Table II., in the first line, Biot's figures are given for their historical interest. He calculated them from an aggregate of the data extant at the beginning of the present century. I cite them from Gehler's *Physik. Wörterbuch* (1825, i. p. 616).

The following line is occupied by the figures calculated by Hallström in 1835 (*Pogg. Ann.* xxxiv. p. 24), when he became

TABLE I.

Direct Results of Observations made upon the Expansion of Water between  $-5^{\circ}$  and  $+100^{\circ}$  C. The volume at the maximum density-point is taken as 1,000,000. Pressure = 1 atm.

$t =$	$-5^{\circ}$	$0^{\circ}$	$+5^{\circ}$	$10^{\circ}$	$15^{\circ}$	$20^{\circ}$	$25^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$	$60^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$	$100^{\circ}$
1. Hallström, 1823...	...	1000108	1000005	1000220	1000786	1001549	1002648	1004025							
2. Muncke, 1828 ...	...	1000111	1000011	1000278	1000671	1001754	1002897	1004272	1007631	1011702	1016424	1021805	1027925	1034930	1043039
3. Stampfer, 1831 ...	1000648	1000113	1000012	1000289	1000606	1001822	1003005	1004418	1007813						
4. Despretz, 1837 ...	1000689	1000127	1000008	1000268	1000875	1001790	1002930	1004330	1007730	1012050	1016980	1022550	1028850	1035660	1043150
5. Pierre, 1847 .....	1000600	1000118	1000008	1000236	1000846	1001712	1002826	1004190	1007631	1011935	1017238	1023059	1029482	1036417	1043773
6. Kopp, 1847 .....	...	1000123	1000007	1000247	1000818	1001690	1002839	1004188	1007655	1011891	1016715	1022372	1028708	1035524	1043114
7. Plücker and Geiseler, 1852. }	1000661	1000115	1000012	1000287											
8. Hagen, 1855 .....	...	1000127	1000010	1000269	1000849	1001721	1002861	1004250	1007711	1011994	1017009	1022675	1028632	1035715	1042969
9. Henrici, 1864.....	...	...	...	...	...	...	...	1004225	1007728	1012068	1017091	1022597	1028697	1035917	1043231
10. Jolly, 1864.....	...	1000126	1000006	1000254	1000846	1001732	1002856	1004239	1007632	1011877	1016953	1022384	1028003	1035828	1043116
11. Matthiessen, 1865 ...	...	...	1000006	1000271	1000802	1001814	1002982	1004345	1007730	1011969	1016984	1022646	1028953	1035813	1043159
12. Weidner, 1866 ...	1000709	1000136													
13. Rosetti, 1869 .....	1000652	1000136	1000006	1000246	1000835	1001742	1002861	1004249	1007738	1011907	1016862	1022529	1028836	1035462	1043116



acquainted with Muncke's and Stampfer's results. But his results were but little known, since Despretz's figures (see Table I.) were published shortly after and attracted general attention. The same remark applies to Kopp and Pierre's figures, published ten years later.

Miller (Phil. Trans. 1856, p. 146), when establishing the relation of the English pound to other units of weight, examined the existing data for the density of water, and having corrected them for the expansion of mercury, he compiled them into a very simple formula, according to which the logarithm to seven places of the volume (reckoning unity at 3°·945), equals

$$32\cdot72(t-3\cdot945)^2-0\cdot215(t-3\cdot945)^3,$$

and his tables (from 0° to 25°) were long used by many investigators. He took Despretz's, Pierre's, and Kopp's data as a basis for his calculations.

Rosetti, taking Despretz's, Kopp's, Hagen's, and Matthiessen's, in addition to his own determinations, calculated the mean regulated values, which are frequently made use of at the present time.

Volkman (Wied. *Annalen*, 1881, xiv. p. 277), adopting Levy's determination (1881) for the expansion of mercury (viz. 0·018207 from 0° to 100°), recalculated the determinations made by Kopp, Pierre, and Jolly, embracing Hagen's and Matthiessen's data, and rejecting those figures which he regarded as being very incorrect, and took an average of all, without, however, subjecting them to any regularization and preferring to remain as near as possible to the empirical results.

Mendeléeff ('Messenger of Commerce,' 1884, and separate work, 'The Investigation of Aqueous Solutions according to their Specific Gravity,' 1887, p. 42), in studying (1880-84) the existing data concerning solutions, made a calculation similar to Volkman's, taking as a basis the expansion of mercury from 0° to 100° as equal to  $0\cdot00018210 \pm 0\cdot0000007$ , which he deduced in 1875 from Regnault's determinations; and, taking into consideration all the figures given by Despretz, Kopp, Plücker and Geissler, Hagen, Jolly, Henrici, Weidner, Matthiessen, Hirn and Rosetti, he calculated the averages, which are given in the table. The figures are, however, only given to hundred-thousandths of the density, without being referred to the hydrogen thermometer, and in the calculation for 20° a mistake occurred, so that this number is not included.

During the current year, Admiral Makaroff (Journal of

the Russian Physico-Chemical Society, 1891, Physical Section, p. 30), in elaborating the vast material collected by him during his voyages round the globe, relative to determinations of the density of sea-water, deduced a formula which expresses the expansion of water between  $-5^{\circ}$  and  $+35^{\circ}$ , employing the compilations of his predecessors, and amongst others of Herr, made for the International Metrical Commission.

To these compilatory data I subjoin (a) the arithmetical mean of all the data of Table I.; (b) the value of  $\frac{dV}{dt}$ , i. e. the increment of the volume corresponding to an increment of temperature of one degree; (c) the value of  $\frac{dV}{dp}$ , or the increment of volume corresponding to an increment of pressure of one atm. (this  $=\mu_t V_t$ ); and lastly (d) the value of the possible error in contemporary determinations of the volumes of water. The numbers in this line were deduced on the basis of the following considerations:—

(1) Since it is conditionally received that the volume at  $4^{\circ}$  equals unity (or  $10^6$ , according to the notation adopted in this table), it follows that at  $4^{\circ}$  the error will be zero, and we may grant that all the errors are proportional to the difference  $t-4^{\circ}$  \*.

(2) Since the existing data are, for the most part, referred to readings of the mercury thermometer, they must contain that error which these readings include if we suppose them corrected in every other respect. The minimum of this error for the best thermometers of hard glass is given above, but I do not think it necessary to add this error to the sum of possible errors, because, in the first place, it can now be to a great extent corrected, and, in the second place, with different thermometers the amount of this error must present a certain unavoidable variability, whose value cannot possibly be now determined.

(3) In the determination of temperatures, the observers have up till now been satisfied with hundredths of a degree, and frequently even tenths, so that, generally speaking, the error for temperatures may be taken as  $\pm 0^{\circ}05$ . However, for temperatures below zero, where there are fewer observations and these more difficult, the amount of this error must

\* Although perhaps the maximum density is not exactly at  $4^{\circ}$ , still it undoubtedly lies between  $3^{\circ}5$  and  $4^{\circ}5$ ; and within this range the volumes of water vary so little, that practically, within the limit of existing errors, this density may be presumed to be situated at  $4^{\circ}$ , all the more so, as all later investigators give it a temperature very near  $4^{\circ}$ , for instance Hagen  $3^{\circ}98$ , Rosetti  $4^{\circ}07$ , Kopp  $4^{\circ}08$ , &c.

be increased; and thus for  $-10^\circ$ , I take it as  $\pm 0.1$ , for  $+20^\circ$  and  $100^\circ$  as  $\pm 0.05$ . By multiplying these values by  $\frac{dv}{dt}$  we get, for  $-10^\circ \pm 26$ , and for  $20^\circ \pm 10$ , and for  $100^\circ \pm 39$  millionths of the volume.

(4) The foregoing examination of the points generally taken as granted in determining the coefficient of expansion of glass, leads to the conclusion that the error in the volume of the vessel will attain at least  $\pm 0.000001$ , which introduces a possible error in the volumes of water of as much as  $\pm (t-4)$  millionths of the volume, because the coefficient of expansion of the vessel enters into the value of the volume of water after being multiplied by the number of degrees.

(5) Inasmuch as, up to the present, no corrections have been made for an alteration in the volume of water due to a change of atmospheric pressure, and since these differences of pressure at various seasons of the year and in different localities may amount to  $\frac{1}{10}$ th of an atmosphere, I hold it necessary to add a possible error of  $\pm 4$  millionths of the volume to the differences of individual observers, for the reason indicated, and equal to  $\mu 0.1$ .

(6) Judging from the description of the methods of investigation and from a comparison of individual observations, we must recognize the existence of errors amounting to ten-thousandths of a volume in the determination of volumes and weights at different temperatures. But the greater portion of possible errors of this category disappear in the majority of cases, when the final results are calculated out (often by the method of least squares). I therefore estimate such an incidental error as not exceeding  $\pm 5$  millionths of the volume in the best extant determinations.

(7) The sum of the errors enumerated above, which have been taken at the lowest possible computation, is equal to  $\pm 49$  for  $-10^\circ$ ,  $\pm 35$  for  $+20^\circ$ , and  $\pm 144$  for  $100^\circ$ , taking the volume at  $4^\circ$  as equal to  $10^\circ$ . Supposing the errors proportional to  $t-4$ , we have, in virtue of the above figures, the following equation :

$$\text{Possible error} = \pm (t-4)(3.0 - 0.0469t + 0.00032 t^2).$$

The values corresponding to this equation are given under heading (d) in Table II.

Since the constants A, B, and C, in formula No. 1 are calculated from existing data, which contain, *at the very least*, the above-mentioned errors, so these errors may also occur in the values given by this formula. However, the best experimental results differ from the numbers given by the formula

in a much less degree, as is seen from the comparison of the volumes thus obtained (last line of Table II.).

In Table III. are cited the results given by formula No. 1, which is here given in the form in which I employed it for calculation :

$$S_t = 1 - \frac{(t-4)^2}{1000\phi(t)},$$

where

$$1000\phi(t) = 1.90(94.10 + t)(703.51 - t),$$

and

$$\phi t = 128.78 + 1.158t - 0.0019t^2.$$

These figures refer to the density of water  $S_t$ , which is inversely proportional to the volumes, *i. e.*  $S_t V_t = 1$ . The density at  $4^\circ$  is taken equal to unity.

In calculating this formula, averages were taken of the determinations of many investigators (Despretz, Kopp, Jolly, Rosetti, Hagen, and Matthiessen), and those of some of them (of the first four observers) were corrected for the expansion of mercury, adopting the value 0.01821 as its variation in volume between  $0^\circ$  and  $100^\circ$ ; but no correction was made for the variation of the coefficient of expansion (mercury and solids) with a variation of temperature, nor for the readings of the mercury thermometer as referred to the hydrogen-scale (since such corrections cannot be considered as uniform or sufficiently investigated at present). The figures, therefore, obtained by the formula may contain the same errors as commonly occur in the existing determinations, and for this reason I have indicated the possible errors in the density in this table. For temperatures below  $100^\circ$ , they are found from the errors in the volumes given in Table II., on the ground that  $dS = \frac{dV}{V^2}$ ; for higher temperatures than  $100^\circ$

they are derived from the considerations set forth in examining the influence of pressure (see *anté*). But although the figures given by the formula may contain errors to the amount indicated, still it is unlikely that they attain, for ordinary temperatures ( $0^\circ$  to  $40^\circ$ ),  $\frac{1}{3}$  or  $\frac{1}{4}$  of the value given, since the difference between the results given by experiments and the formula is much less, between  $0^\circ$  and  $40^\circ$ , than the amount of the possible errors. Thus, for instance, for  $15^\circ$  we obtain a density 0.999152 or a volume 100849, which differs from the mean results of Volkmann, Rosetti (Table II.), Jolly, and Hagen by less than  $\frac{1}{4}$  of the error, which is admissible in the existing data on the grounds stated above. Such being the case we may take the results given by the formula between

TABLE II.

Mean Values (corrected in accordance with contemporary data) for the Expansion of Water with a Change of Temperature, from  $-5^{\circ}$  to  $+100^{\circ}$ , taking the volume at  $4^{\circ}=1,000,000$  and the pressure = 1 atm.

	$-5^{\circ}$	0	$+5^{\circ}$	$10^{\circ}$	$15^{\circ}$	$20^{\circ}$	$25^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$	$60^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$	$100^{\circ}$
Blot, 1811 .....	...	1000130	1000002	1000186	1000694	1001486	1002562	1003911	1007387	1011832	1017161	1023298	1030148	1037629	1045668
Ballstrom, 1835 .....	...	118	016	263	838	1721	2890	4336	7616	11680	16518	22040	28193	34913	42139
Müller, 1856 .....	...	...	008	265	854	1739	2882								
Rosetti, 1871 .....	1000702	1000129	010	253	841	1744	2888	1004260	1007700	1011860	1016910	1022560	1028670	1035670	1043120
Volkman, 1881 .....	...	122	008	261	847	1731	2868	4260	7700	11970	16940	22610	28610	35740	43230
Mendeleeff, 1884 .....	...	130	...	260	843	...	2868	4248	7700	11962	16948	22651	28683	35710	43252
Makarov, 1891 .....	1000688	121	1000008	262	846	1727	2870	4243							
(c) Mean of data in Table I. ....	1000662	1000122	1000002	1000263	1000847	1001738	1002871	1004248	1007700	1011838	1016915	1022518	1028649	1035719	1043180
(b) $dV/dt$ for 1 degree ...	-157	-66	+15	+85	+148	+204	+254	+302	+386	+461	+530	+586	+656	+719	+781
(c) $dV/dp$ for 1 atm. ....	-52	-50	-48	-47	-46	-45	-44	-43	-41	-40	-39	-40	-41	-42	-44
(d) Possible error of existing determinations	$\pm 29$	$\pm 12$	$\pm 3$	$\pm 15$	$\pm 26$	$\pm 35$	$\pm 43$	$\pm 49$	$\pm 69$	$\pm 67$	$\pm 75$	$\pm 85$	$\pm 98$	$\pm 118$	$\pm 145$
Formula No. 1. $1/S_t = V_t =$	1000676	1000127	1000008	1000262	1000849	1001731	1002880	1004276	1007725	1011967	1016926	1022549	1028811	1035692	1043194

0° and 40° to be very probable. We have already seen the remarkable concurrence of the formula with Hirn's data for temperatures above 100°; so that from both sides—for the lowest and the highest temperatures—the applicability of the formula to the reality is quite likely; and the results given by it are not less trustworthy than the averages deduced from experiments.

With respect to temperatures between 40° and 100°, the evidence of investigators is more conflicting than could be desired, and than is called for by the value of the possible errors given in Table II. For instance, at 70° the difference of the volumes observed by Jolly and Matthiessen amounts to 204 millionths, and the volumes observed by Kopp and Pierre differ by 687 millionths, whereas the possible error at 70° given in Table II. only amounts to  $\pm 85$  millionths. But the volume at 70° given by the formula (1022549) differs from the general average (1022513) by only 36 millionths, and from Rosetti's experimental result (1022529) by only 30 millionths, and occupies a position among the results given by Jolly, Matthiessen, Kopp, Pierre, Hagen, and Despretz: it is, therefore, more probable than the figures of any one of these observers, and even more likely to be true than the average result, for the very reason that the formula satisfies alike the data for 70° and for higher and lower temperatures. In other words the figure shown by the formula for, say 70°, is confirmed not only by experiments made at 70°, but also by determinations at 0° or at 200°.

Besides the specific gravity, calculated by the formula and given in the second column, and the measure of the errors, which probably will not be exceeded in more accurate fresh determinations, Table III. contains the following quantities:—

(a) The differential coefficient  $\frac{ds}{dt}$  found from the formula.

The values of this differential coefficient are not only useful practically in calculating results for intermediate temperatures, they not only demonstrate the mode of variation of the density of water, but they also present, in my opinion, a great theoretical interest, because natural phenomena, in their differential expression, always become simplified and easier to study. It appears to me to be highly instructive that the differential coefficient  $\frac{ds}{dt}$  for lower temperatures gives a line of considerable curvature, but for higher temperatures asymptotically approaches a straight line, which circumstance I propose to take advantage of hereafter, for certain deductions relative to the expansion of aqueous solutions and of various other liquids.

(b) The differential coefficient  $\frac{ds}{dp}$ , or the variation of the

density of water with an increase of pressure equal to one atm. The numbers in this column are calculated by formula No. 7, and only represent a first rough approximation on this subject, and none at all for temperatures above  $100^{\circ}$ . Nevertheless I considered it useful to cite these figures in order to point to the necessity, when making accurate determinations of the variation of the density of water, of paying attention to the pressures at which these determinations are made. If  $\mu_t$  be given, then  $\frac{ds}{dp}$  will be found by multiplying by  $S_t$ .

(c) The values of  $\phi(t)$  or  $\frac{(t-4)^2}{1-S_t}1000$ , because these numbers, as explained above, served chiefly in deciding the proposed formula for expressing the expansion of water.

TABLE III.

The Variation of the Specific Gravity of Water  $S_t$  from  $-10^{\circ}$  to  $+200^{\circ}$ , taking  $S_t=1$  at  $4^{\circ}$ , according to the formula

$$S_t = 1 - \frac{(t-4)^2}{1000\phi(t)},$$

where  $\phi(t) = 1.9(94.1+t)(703.5-t)$  at a pressure of 1 atm.

$t^{\circ}\text{C.}$	Calculated specific gravity, $S_t$	Possible error of existing determinations in millionths.	Pressure Differential Coefficient $ds/dt$ per degree Celsius in millionths.	Temperature Differential Coefficient $ds/dp$ per atmosphere in millionths.	Value of $\phi(t)$ .	Volume, $V_t$ .
-10	0.998281	$\pm 49$	+ 264	+54	114.01	1.001722
-5	0.999325	29	+ 157	+52	119.94	1.000676
0	0.999873	12	+ 65	+50	125.78	1.000127
+5	0.999992	3	- 15	+48	131.52	1.000008
10	0.999738	15	- 85	+47	137.17	1.000262
15	0.999152	26	- 148	+46	142.72	1.000849
20	0.998272	35	- 203	+45	148.18	1.001731
25	0.997128	43	- 254	+44	153.54	1.002880
30	0.995743	49	- 299	+43	158.81	1.004276
40	0.992334	53	- 380	+41	169.06	1.007725
50	0.988174	65	- 450	+40	178.93	1.011967
60	0.983356	72	- 512	+39	188.42	1.016926
70	0.977948	80	- 569	+39	197.53	1.022549
80	0.971996	92	- 621	+40	206.26	1.028811
90	0.965537	109	- 670	+41	214.61	1.035692
100	0.958595	133	- 718	+42	222.58	1.043194
120	0.943314	600	- 810	+43	237.38	1.060093
140	0.926211	650	- 901	+48	250.66	1.079667
160	0.907263	700	- 995	+55	262.42	1.102216
180	0.886393	750	- 1093	+64	272.66	1.128167
200	0.863473	800	- 1200	+73	281.38	1.158114

(d) In the last column the volumes of water, taking that at  $4^{\circ}$  as unity, are given. These volumes, like all the numbers deduced from formula No. 1, are referred to a pressure of one atmosphere. In order to obtain the volumes at a pressure of  $p$  atm., we must divide the numbers in the table by

$$1 + \mu_t(p-1),$$

just as was done previously when examining Hirn's figures.

In conclusion, I think it necessary to repeat that, whenever I am able I shall endeavour to make a series of fresh determinations, taking into consideration all the necessary conditions of the variation of the density of water with a change of temperature, because the sum of modern information on this subject has been already amassed, but suppositions have been admitted (for example, the constancy of the coefficient of expansion of glass and mercury irrespective of a change of temperature, the absence of the influence of pressure, &c.), which cannot be held to agree with our existing knowledge. And should fresh determinations, made with all possible accuracy, confirm the aspect of the formula

$$S_t = 1 - \frac{(t-4)^2}{(A+t)(B-t)C},$$

or lead to a more correct formula, then we may hope by its means to arrive at a better understanding of the true law of the expansion of all liquids, and consequently of gases also. The correct idea of the influence of heat on densities and volumes began with the study of water, and, in my opinion, we may expect, by means of investigations upon water, to make further progress in the study of matter under the influence of a rise of temperature.

St. Petersburg, April 1891.

## XII. *The Densities of Sulphuric-Acid Solutions.*

By SPENCER UMFREVILLE PICKERING, F.R.S.\*

A SHORT time ago Mr. Lupton (Phil. Mag. xxxi. p. 424) attempted to disprove one of the changes of curvature in the figure representing my "first differential" of the densities of sulphuric-acid solutions by bridging it over by a straight line. As, however, this figure is evidently curvilinear, it was not surprising that he failed, even though he selected for the attempt that particular change which, as I had pointed out, was more doubtful than any other (that at 58 per cent.), and for the same reason it is evident that he would

\* Communicated by the Author.



have met with better success if he had tried to bridge it over with a curve instead of a straight line\*. This Prof. Rücker has recently succeeded in doing in a very ingenious manner (Phil. Mag. xxxii. p. 304): but here, I venture to think, his success comes to an end: for I believe that I can show that, so far from his having disproved the three other of my breaks over which his calculations extend, his arguments do not at all affect one of them, while they afford additional evidence in favour of the remaining two being in reality points at which some changes occur in the nature of the solution.

Before giving my reasons for this opinion, I must state most emphatically that even the most successful attempt to afford an alternative representation of a restricted portion of the experimental results can, in my opinion, do but little towards upsetting conclusions which are founded entirely on the cumulative evidence derived from independent sources, and for the establishment of which, as I have insisted repeatedly, no single score of determinations, nor even a whole series of results with any one particular property, would have been sufficient. Prof. Rücker says that "as [my] work covers a wide area, [I] cannot complain if those who study [my] method devote themselves particularly to some one application of it" (p. 304). This may be true; but those who do so cannot bring forward their results as an argument against conclusions which depend entirely on the concordance of independent evidence, and not on any one particular application. If my critics could show that the same alternative interpretation which they suggest in the one case that they investigate is possible in every case, or even in a large number of the cases, and is as consistent with the experimental data as mine was, then, and then only, would their argument be a weighty one.

That part of the cumulative argument for the existence of changes in sulphuric-acid solutions at certain percentages, which was embodied in my paper on the nature of solutions (Chem. Soc. Trans. 1890, p. 64), has already appeared in the pages of this Magazine (xxix. p. 427); but the very remarkable confirmation of my previous results obtained by a study of the freezing-points of such solutions *made after the former paper*

\* In a note in the 'Chemical News' (vol. lxiv. p. 1) I said that a single curve would not bridge over this break without an allowance of ten times the known experimental error. This was wrong. What I had in my mind, and what I ought to have said, was that a curve of the form used by Mr. Lupton—a straight line in the "differential"—would not do so; in fact the error of .000087 which I mentioned was that which Mr. Lupton's equation gave when compared with the experimental points.



solutions at the points indicated, and strong evidence that their occurrence had an intimate connexion with the existence of a corresponding hydrate. Wishing, however, to make assurance doubly sure I carried out, *after my first paper was written*, a series of experiments on the freezing-points. The isolation of the tetrahydrate, whose percentage corresponds to one of the most feebly marked of the changes which I had previously discovered, amply justified my view of their connexion with hydrates; but the entire agreement of the minor changes, marked  $\odot$  on the diagram, with those previously found was perhaps even more satisfactory. Of the thirteen changes previously found to exist between 2 and 98 per cent. nine were confirmed, while as regards the others, which were situated in regions of very low freezing-point, data were either insufficient or entirely lacking.

Remembering that the results set out above were obtained by the application of the same method and the same form of curves to figures which in the majority of cases differed entirely from one another in general form, the question arises as to how such concordance could have been obtained. If we refuse to conclude that the results are due to some property possessed by all the figures in common of exhibiting changes of some sort at these points, we are driven, I think, to explain it in one of the three following ways:—(1) That I knowingly “cooked” my results—an explanation which has not yet been offered; (2) that I did so unconsciously; which would seem to be quite impossible, owing to the properties studied being entirely different, and to my having obtained the same results with every different form of plotting and on every different scale\*; or (3) (which is obviously absurd)

\* I may mention a very strong proof of how independent my results are of any unconscious “cooking,” and of the particular form in which the data are presented for examination. I received a short time ago from my friend Mr. Hayes a series of numbers which I took to be what I was at the time expecting from him—namely, a set of imaginary experiments constructed from equations, with a view to seeing whether I would find out the points at which the equation had been changed. After sending him the results of my examination, I learnt that the values sent were my own experimental results for the densities at 18° from 95 to 19 per cent., metamorphosed beyond recognition, and I also learnt that I had correctly located the breaks which I had mentioned in my published work. The results were

92,	85.6,	79.7,	{ some breaks, but position uncertain }	49.6,	and 30.4 per cent.; as
against 93.6,	84.5,	78.0,	72.8, 58,	51.0,	and 29.5 per cent. formerly given.

The values which Mr. Hayes sent to me were  $x=1250(100-p)$ , and  $y=10^6 \cdot \frac{1}{s^2} \cdot \frac{ds}{dp}$  ( $p$  = percentage, and  $s$  = density).

The data for finding the first of these breaks were more meagre than they should have been, and a note was made by me that its position might be at a percentage higher than 92.

that the arrangement of points exhibited by the diagrams is purely accidental.

Setting aside for a moment the concordance of independent results, and thus ignoring the main grounds of my conclusions, let us see what Prof. Rücker's results do towards disproving my opinions in the one particular case which he investigates.

I may as well state at once that I consider Prof. Rücker's equation to agree with the experimental results just as satisfactorily as my own drawings do, and more satisfactorily perhaps than he asserts; for I have recently revised my estimate of the experimental error, and obtain a value for it somewhat larger than I previously did. From all my determinations done in duplicate with water I get  $\cdot 000012$  ( $\cdot 0003$  gram on the 25 cubic centim. taken) as the *mean* error of a single observation, and, by a graphic method, described by me in the *Ber. d. deutsch. chem. Gesel.* (xxiv. p. 3332), applied to the results with sulphuric acid itself, I get  $\cdot 000011$ . This agrees perfectly with my original drawing, which attributed an apparent error of  $\cdot 000013$  to the experimental points (due allowance being made, of course, for the fact that these were "differential" points, of which the error would be sometimes greater and sometimes less than that of a single determination, according to the magnitude of the actual differences taken), and equally well with Prof. Rücker's equation, which gives  $\cdot 000012$ .

Now, as is well known, any figure, however complicated, may be expressed by an equation, within any assigned limits of accuracy, even of the simple form  $y = a + bx + cx^2 \dots + zx^n$ , provided a sufficient number of terms be introduced into it, and this is true even if the available points form in reality two distinct parabolas or other curves. This Prof. Rücker himself points out to be the case (p. 305); so that the mere fitting on of an equation is no proof of continuity. The task of finding an equation to fit fairly well on to a figure made up of such independent curves is naturally more simple when these curves meet almost "end on," if I may use such an expression, and show no changes of so marked a character as to be correctly described as violent and sudden, or as presenting any "awkward corners." Such is the nature of that portion of my density-differential curve selected by Prof. Rücker for examination; the changes of curvature which I suppose it exhibits are, as he admits, "minor changes," and by no means so clearly indicated as some of those in other parts of the figure; and in such a figure it would evidently be possible, by taking mean points between each pair of experimental points, to get an equation, even of the simple para-

bolic form, with seven constants, to agree very closely indeed with fourteen of the points; and the number of points with which an equation could be made to coincide might be further increased considerably by the fact that eight of the points lie very nearly on a single straight line. When to these considerations we add that of an operator of the highest skill and ingenuity, it would indeed be remarkable if Prof. Rücker's seven-constant equation did not show a very close agreement with the twenty experimental points investigated. I say *twenty* points advisedly, for of the twenty-four points inserted by Prof. Rücker, four (those at 80.04, 79.12, 65.12, and 57.94 per cent.) are deduced from determinations (by taking alternate experiments) which have already been used to their full extent in supplying the other points given in his tables.

But Prof. Rücker has not confined himself to the use of the parabola or any other simple equation, but has used an equation of a complex and highly artificial form, for which, I believe, there is no precedent, and for which, as an expression of physical facts, there would seem to be (I speak under correction) no probability whatever. Prof. Rücker first finds an equation (a combination of an exponential curve with a straight line)  $y = a + bx - cd^x$ , which agrees well with two or three experimental points between 47 and 51 per cent., and again with those between 72 and 80.5 per cent., these two portions constituting together but  $\frac{2}{10}$ ths of the total length of the figure. For all solutions weaker than 47, and stronger than 80.5 per cent. there is no semblance of an agreement; and the whole of the middle portion of the curve between 51 and 72 per cent. "lies a little below that given by experiment," and cannot therefore be accepted as a representation of the experiments. In order to rectify this defect and to raise this portion of his curve, Prof. Rücker ingrafts on to it a "hump" by means of a fourth term,  $m/(n^x + n^{-x})$ . Now it is obviously possible in the case of any figure such as that under discussion, where any changes of curvature which exist are by no means very abrupt, but are only "minor changes," to mould a curve to the exact form of the experimental figure, if it is lawful to pare it down, or plaster it up wherever it may be necessary\*, and the mere fact of obtaining such an equation to fit can, I maintain, prove nothing beyond the skill of the operator.

Even, however, if such an operation could disprove the existence of breaks, Prof. Rücker's estimate of the number of my breaks which he has disproved would have to be materially reduced.

\* For the whole of the density-results an equation of this sort would at a moderate estimate contain about 21 constants.

His equation extends from 80.5 to 46.9 per cent. (the values are given below in Table I., which is mainly a reproduction of Prof. Rücker's Table I.), and my breaks occurred at 78,

TABLE I.

$p$ .	$(a+bx-cdx) \times 10^6$ .	$m/(n^x+n^{-x}) \times 10^6$ .	$\beta - a$ .	$\gamma - a$ .
80.54	11130		+13	+32
79.48	11354		-46	-55
78.62	11490		+64	+52
77.11	11659	1	-13	-18
74.98	11764	2	+13	+27
73.01	11766	3	+ 2	0
71.06	11703	5	0	-14
69.10	11594	10	+ 9	- 4
67.12	11452	17	+ 2	- 8
65.51	11319	27	+35	+23
64.50	11229	34	-72	+87
63.08	11097	46	+16	- 6
61.01	10893	55	+12	-18
58.94	10681	46	- 4	-29
56.89	10466	30	+30	+14
54.89	10251	17	- 7	-18
52.91	10037	10	- 7	-18
50.91	9817	5	+11	+ 5
48.91	9596	3	0	+ 3
46.94	9379	2	1	+19
Average error in density .....			12	15

72.8, 58, and 51 per cent., so that the calculations extend but 2.5 per cent. beyond the first of these breaks\*, a distance wholly insufficient to disprove anything about a break, the position of which can be determined only with "extreme difficulty to within 1 or even 2 per cent." (Chem. Soc. Trans. 1890, p. 126). In the same way little can be concluded as to the break at 51 per cent., for although the calculations extend 4 per cent. beyond it, they embrace only 2 experimental points in this length†. That the calculations do not really bridge over these two breaks to any appreciable extent, is clearly shown by the fact that on extending them for any distance beyond the points taken they at once begin to leave the experimental values. I, therefore, must take the most decided exception to Prof. Rücker's statement that his one curve can act as a

\* In some cases the position given for this break was as high as 79 per cent, or only 1.5 per cent. from the end of Prof. Rücker's curve.

† In some cases the position given for this break was as low as 49 per cent., or 2 per cent. from the end of Prof. Rücker's curve. The mean position was 49.9 per cent.

substitute for my five discontinuous curves (pp. 308, 310); it does *not* do so; all that it does is to cover three of my curves, and small, altogether insufficient portions of two others.

This leaves but two breaks which could possibly be materially affected by the calculations, and one of these I certainly would never have ventured to uphold on the strength of this one series of results, for the only conclusion which I drew respecting it, even from the four concordant series of density determinations at different temperatures, was that it was "of a very doubtful character" (*loc. cit.* p. 76), so that the calculations can be said to materially affect but *one* of the breaks whose existence I asserted—that at 72·8 per cent.: and what evidence does it afford respecting this one?

The hump in Prof. Rücker's equation begins to be appreciable at a certain point, and again becomes inappreciable at another point, and if the quantities constituting it have any physical meaning at all, they must mean that a certain substance is present, or that certain physical conditions exist, to an appreciable extent between these points only, and are altogether inappreciable throughout the whole of the rest of the solutions, whether stronger or weaker. This is precisely what occurs with a hydrate, according to my views. But let us go further and see at what points this temporary disturbance begins and ceases. Without much error we may say, I think, that any deviation would first begin to be practically appreciable when it attained a magnitude of about  $\frac{1}{4}$  to  $\frac{1}{2}$  that of the mean experimental error, say  $\frac{1}{2}$ ; this would be  $4 \times 10^{-6}$  in the present case; and the point at which the fourth term in the equation attains this magnitude is 72 per cent., almost the exact point at which my break occurs, +72·8 per cent.; and, further still, it diminishes to this magnitude, and again becomes inappreciable, at 49·9 per cent., just where another of my breaks occurs—51 per cent. in the present series of experiments, 49·9 per cent. in the mean of all my experiments. I should, however, not place much value on the concordance in this second case, owing to Prof. Rücker's equation extending such a short distance beyond this point. We are forced, I think, therefore, to regard Prof. Rücker's results as affording additional evidence in favour of my principal contention—the practical starting of a fresh order of things at certain definite points. In fact, the only dilemma on to the horns of which Prof. Rücker's results have placed me is, not that which he imagines (*loc. cit.* p. 313), but that of having to decide whether the graphic or mathematical method is best suited for discovering those points at which practical changes in solutions occur.

Prof. Rücker admits that "the curves in some parts—if not discontinuous—have peculiar features which suggest special physical causes : " his "doubts have always had reference to the minor changes of curvature," such as those here discussed, "and to the use of the ruler in detecting them." He certainly does not appear, however, to have done much to justify these doubts ; for however we may differ in our explanations of these changes, or of the relative degree of suddenness with which they occur, he must admit that I with my bent ruler have as a matter of fact discovered the exact points at which he with his mathematics has found that a fresh order of conditions becomes appreciable, and again disappears.



Prof. Rücker would, no doubt, point out that, although the fourth term in his equation is appreciable throughout a certain range only, it is not actually non-existent in other parts, and that, therefore, there is no true mathematical discontinuity. I never, however, ventured to assert that the changes occurred so suddenly as to prove strict mathematical discontinuity ; and I fail entirely to see how such discontinuity could ever be proved or disproved by any experiments which were not absolutely free from experimental error, and which were not infinite in number. Indeed, those hydrates, the presence of which in appreciable quantities conditions a particular rate of change of density &c. between certain points, cannot be regarded as being entirely absent from other solutions—a view which the principles of dissociation and the gradual removal of such hydrates or substances in the solid or gaseous form from such solutions necessitate (see Chem. Soc. Trans. 1889, pp. 22, 23; 1890, pp. 138, 340)—the only statement which we can make on the strength of experiments is that the amount of the substances present is inappreciable, or otherwise, by those experiments. In the same way the suddenness with which a change of curvature occurs can only be determined within limits comparable with those of the experimental error. My "breaks," in fact, are similar to those which we get in most cases of a change of condition, where the practical existence of the break is beyond doubt, although its absolute abruptness may always be doubted, and could certainly never be proved in a strictly mathematical sense.

Again, it might be urged that if in a series of experimental results such as the present the practical disappearance of any term in a continuous equation devised to represent them occurs at any particular point (as Prof. Rücker's fourth term does at 72 per cent.), it would not cease to be appreciable till some other point were reached if the accuracy of the determinations were increased, say, tenfold. This is as it may be : but it is useless to speculate as to what might be the case with



experiments of such accuracy, for we do not know whether the present equations would still be applicable without modification.

As to the uncertain break at 58 per cent. which Prof. Rücker's equation successfully bridges over, I may point out that even here my failure to recognize the sensible continuity of the figure cannot be attributed to any fault in the method, but to one in the operator. I invariably used the lath bent

into the simplest form, , whereas, by applying the forces in a different manner it can be bent into the wavy form, , and when bent into this latter

form I now find that it will fit over the supposed change at 58 per cent. ; but it may be remarked that if we adopt this interpretation of this portion of the figure we shall not get a straight line on differentiation ; and as the bulk of evidence goes to show that the second differential is sensibly rectilineal throughout the figure (a fact to some extent recognized by Prof. Rücker, pp. 306, 307), it is probable that this one portion would be of a similar nature, and that the interpretation of it as a wavy curve would be erroneous—a view which seems all the more probable from the indications of changes at this point in the case of other properties at this same relatively high temperature, and from the existence of a break in the freezing-points at low temperatures, which I think no one would venture to question, even if the corresponding hydrate had not actually been isolated. The present case of the densities is the only one I believe in which a wavy curve might be substituted for two of my simpler curves.

A wavy parabola can be found to bridge over the break at 58 per cent. as well as a wavy bent-lath curve, and in this way the whole portion of the figure examined by Prof. Rücker may be represented by two parabolas, and the use of just as many constants as are required by Prof. Rücker's equation ; the errors according to the two drawings are, moreover, nearly equal ( $\beta - \alpha$  in Table I. are the errors according to Prof. Rücker's equation,  $\gamma - \alpha$  the errors according to the parabolas\*), so that the magnitude of the error

\* The parabolas are  $y = \cdot 011767 + \cdot 00008782x - \cdot 00001588x^2$ , and  $y = \cdot 011767 + \cdot 00002917x - \cdot 00000442x^2 - \cdot 0000000789x^3$ ,  $x = p - 73$ . The constants have been deduced from the readings of a curve instead of directly from the experimental values, and the average error is, consequently, rather larger than it would otherwise have been. It would in any case be somewhat larger than that according to my original drawing, for the equations extend a short distance beyond the points at which I believe breaks occur, namely, 51 and 78 per cent.

will not help us to decide between their respective merits: but whereas Prof. Rücker's equation is artificial and is a very improbable representation of physical facts, the parabola is a form of curve which has been found to express physical facts "in the great majority of cases in physics and chemistry" (Lupton, *loc. cit.* p. 421), and for the application of which in the present case we have the theoretical considerations advanced by so high an authority as Mendeléeff\*. Considering, moreover, that the mathematical continuity expressed by Prof. Rücker's curve does not even help us to assert that there is not a change in the nature of the solutions attaining recognizable dimensions just at the point where the parabolas indicate that such a change occurs, we can, I think, have but little hesitation in making a choice in favour of the latter.

Two points of minor importance remain to be noticed. On p. 310 Prof. Rücker suggests that errors, similar to those which I found in making up solutions from two different lots of stock acid, may exist in making up different solutions from the same stock lot. This, I think, is surely not the case; for in using different samples of acid the results depend on the comparison by analysis, or by some other means, of the strength of the two, and this cannot be done with an accuracy in any way approaching to that attainable by mixing weighed quantities of two substances.

Prof. Rücker alludes to my having omitted certain points which I considered exhibited exceptionally large errors, while I insisted on changes dependent on differences of smaller amount. In dealing with a "differential" figure, an error in one of the experiments affects two consecutive differential points in the opposite direction, making them too high and too low respectively; and it is only in cases where this appearance is evident that we should be justified in assuming, provisionally at any rate, the existence of an exceptional error. It was only in such cases that I assumed it; but at the same time I quoted fully the determinations which I considered to be erroneous, so that others might use them in whatever way they thought fit. These questionable determinations should, no doubt, have been repeated, but to do this in every case would have meant an additional amount of work which would have been prohibitory. It was open to me to obtain evidence in favour of my views either by the study of one or two cases worked up to the highest pitch of perfection, or to accumulate a considerable mass of less perfect instances from independent

\* Chem. Soc. Trans. 1887, p. 778. Mendeléeff concluded that the parabolas would have one term less than my work would show them to have; this was due, no doubt, to his having assumed that the various hydrates present were practically undissociated.

sources. I thought the latter was the preferable method, and adopted it.

On p. 311 Prof. Rücker says :—"Why, for instance, are we to admit an error of 22, or three times the lower limit to the maximum error, at 56.89 per cent., and insist that an error of 16, which is only twice the same limit, is impossible at 63.08 per cent.?" Such a question is open to serious misconstruction, for I neither rejected nor specially insisted on either of these experimental points, but quoted them without comment in my tables, and inserted them in my diagrams, treating and accepting both of them to exactly the same extent.

In forming an estimate of how far a criticism like that now under discussion, based on the examination of a limited portion of one set of my results, can upset my conclusions, it is necessary to bear in mind the exact nature of these conclusions. From the study of any one, or any few, particular breaks, I concluded—*nothing* : from a study of a whole series of density-results I only concluded that it was advisable to make other series at other temperatures : from the study of the series at four different temperatures my conclusions were merely that I had "strong presumptive evidence" of the existence of changes (p. 79), but that confirmatory evidence from the study of independent properties was necessary before such changes could be regarded as established ; and it was only after obtaining such evidence from the study of three or four other properties that I ventured to call this evidence proof, and then only with the oft-repeated caution "that many of these changes were admittedly of a very doubtful nature." When, further, it is remembered that those who have called my conclusions in question have confined their attention to a limited portion of one particular series of results (and that portion one which I myself pointed out to be most open to attack), or have even selected only one particular and excessively doubtful break ; that in spite of this, they have, while adding confirmation to my conclusions in every other respect, only succeeded so far as to bring some additional evidence against (without altogether disproving) the one change which I myself never regarded as proved ; remembering all this, I cannot fail to believe that my conclusions were better founded, and my method of working more trustworthy, than I had ever imagined.

October 1891.

#### POSTSCRIPT.

I have made a detailed examination of several breaks by the bent-lath method, and also by the application of parabolic

equations deduced mathematically from the experimental values, and have found that both methods lead to precisely the same conclusions as to the existence and position of the breaks. The publication of these results has unfortunately been delayed, but the partial examination of one case by the two methods will be found in the *Ber. d. deutsch. chem. Ges.* xxiv. p. 3334.

Since writing the above my attention has been called to the fact that Prof. Lunge has questioned the accuracy of my sulphuric-acid density determinations (*Journ. Soc. Chem. Ind.* 1890, p. 1017). His criticism is based entirely on his own misrepresentation of the facts of the case. My answer to him will be found in the *Chem. News*, vol. lxiv. p. 311.

December 18, 1891.

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### XIII. Notices respecting New Books.

**SOLUTIONS; being the Fourth Part of a Text-Book of General Chemistry.** By W. OSTWALD, Professor of Chemistry in the University of Leipzig. Translated by M. M. PATTISON MUIR. London: Longmans, Green, and Co. 1891.

**A**MONG the many problems which lie on the borderland of Physics and Chemistry, undoubtedly the one of greatest importance, and at the same time one of the most difficult, is the construction of a theory to account for all the known properties of bodies in the liquid state. The chemist, recognizing that the liquid state is most favourable, if not absolutely essential, to the occurrence of chemical reactions, hopes to obtain from such a theory an insight into the nature of chemical affinity and some knowledge of the arrangement of atoms in a molecule. The physicist, on the other hand, regarding the same question from a mechanical point of view, expects that the theory will enable him to ascertain the magnitudes of the forces which act between and within molecules; and, further, by a consideration of the phenomena of electrolysis, he hopes to throw some light on the nature of electricity.

As soon as the laws of gases had been experimentally demonstrated, it occurred to physicists that these might be deduced by considering the molecules of a gas as small hard particles in rapid motion, constantly in collision with each other, and exchanging their velocities during such encounters. The fact that all gases behaved in an exactly similar manner indicated that their particles were so small in comparison with the distances between them, that all the relations of pressure, temperature, volume, &c. might be considered as resulting from forces due to this motion. On compressing gases, however, so that the condition of relatively great separation of the molecules no longer exists, a new set of forces is brought into play, the mutual actions, namely, of the molecules themselves. These forces cause the molecules to cling or cohere

together, and thus the force exerted on any particle of the gas is the sum of the forces due to the motion of the surrounding gas and the cohesion-pressures produced by the molecules in its neighbourhood, these latter depending on the nature of the molecules as well as on their distance apart. The result is that different gases show unequal deviations from the laws of a perfect gas; and by compressing them sufficiently the cohesion-pressure is increased until they finally become liquids. Van der Waals, proceeding on an assumption, which he justifies, that these cohesion-pressures, whatever be their absolute magnitude, must be proportional to the square of the density of the gas, has elaborated a theory of gases which accounts for the phenomena observed during their liquefaction, and offers the most complete explanation of their behaviour which has yet been given.

In order to obtain a more exact knowledge of these cohesion-pressures, observers began to study the properties of liquids, and more especially of solutions of solids in liquids. During the past ten years much work has been done, and a completely new theory of solutions has been started by van 't Hoff, Arrhenius, Ostwald, and other workers on the Continent. The object of the present treatise is to give a concise account of this theory, of the evidence on which it is based, and the results to which it leads.

The older theories of solution are all based on the assumption that the solvent and dissolved substance form definite chemical compounds or hydrates, and therefore that the molecules of the solution have a very complicated structure. The structure of these molecules will change abruptly from one hydrate to another as the amount of dissolved substance is increased; and so the properties of the solutions will undergo similar sudden changes. The presence of such discontinuities in curves of density, freezing-point, and other properties as related to concentration, has been vigorously asserted by Mr. S. U. Pickering in the pages of this Magazine, whereas the upholders of the new theory deny the existence of any discontinuity.

According to the new theory, the molecules of the dissolved substance behave quite independently of the solvent, the latter playing an extremely subsidiary part. In addition to this, if the solution be a dilute one the molecules of dissolved substance act independently of one another, because of their relatively great distance apart. They are just like the molecules of a perfect gas. If we take a partition which is permeable by the solvent and not by the dissolved substance, the difference of pressure on its two faces, when one side is in contact with pure solvent and the other with solution, is due to the bombardment of the partition by the molecules of the dissolved substance. Hence osmotic pressure, as it is called, is accounted for. Similarly the extra pressure due to these moving molecules will cause the freezing-point and vapour-pressure of the solution to fall below those of the solvent. In all these cases the properties of the solution will depend on the number of dissolved molecules and not on their constitution; so that

*Phil. Mag.* S. 5. Vol. 33. No. 200. Jan. 1892. L

chemically equivalent quantities of different substances will produce the same effect in solution. As we proceed to stronger solutions the molecules get closer together, and the theory launches out with the bold assertion that Van der Waals's modification of the law of gases is applicable to the molecules of a dissolved substance also; and the deviations of the properties of a solution from absolute proportionality to the amount of dissolved substance present are calculated on this assumption, the agreement being in some cases remarkably good.

The theory supposes that the molecules of the dissolved substance remain intact when they enter into solution. In the case of solutions of salts the laws indicated above are not obeyed, and the explanation given is that the molecules of the salt split up into their constituent atoms, a view which is supported by many phenomena of electrolysis. Hence the solution contains molecules of salt and free atoms or "ions" which have been produced by the dissociation of the salt. No quantitative measurements are given, because we have no certain knowledge as to the relative amounts of dissociated and undissociated salt. Recently Arrhenius has worked in this direction with some success.

In this treatise the case of salt-solutions is only treated in a somewhat superficial manner; indeed it is at this point that the subject becomes a most difficult one. One hardly justifiable assumption is that the solvent remains inert, although the dissociation of the salt is effected by it. Again, there are chemical objections to having free atoms in a liquid, though Prof. Ostwald suggests very reasonably that a free atom and a molecule of an element are not alike, and do not necessarily have similar properties. An attempt is made to account for many physical properties of solutions by supposing them due to the presence of the ions; for example, colour and refractive indices. It is argued, for instance, that all salts containing a cobalt ion are red, and that therefore the cobalt ion has a red colour; similarly, the copper ion has a blue colour. This law will, however, not admit of universal application; an exception may be seen in the case of ferric sulphocyanide, which is of an extremely deep red colour in aqueous solution, although neither the ferric ion nor the sulphocyanogen one has this colour. The only explanation possible is that the salt is deep red when in the molecular state. In that case a very dilute solution should be orange-coloured, owing to the mixture of the red molecular salt and the yellow ferric ion, of which the latter would be present in the greater quantity.

As a concise account of the new theory of solution Prof. Ostwald's work is most valuable; but it is somewhat to be regretted that he did not give some indication of the older theories, of which not a word is said. Indeed, a student taking up the book and having no previous knowledge of the subject would be led to suppose that the theory here put forward is the universally accepted one, whereas it is really regarded by the majority of chemists as quite untenable.

The translation is an admirable one, and our thanks are due to Mr. Pattison Muir for introducing the work to English readers. One alteration might be suggested for a future edition, to suit fastidious mathematical readers, namely the notation used for logarithms throughout the book. It would be more in accordance with English custom to write for the natural logarithm of  $x$ ,  $\log_e x$  instead of  $l x$ , the latter being a too faithful translation of the original German formula.

JAMES L. HOWARD.

*Index of Spectra. Appendix B. By W. MARSHALL WATTS, D.Sc., F.I.C., Senior Physical Science Master at the Giggleswick Grammar School. Manchester: Abel Heywood and Son, 1891.*

THIS pamphlet of forty pages appears as an appendix to the author's previous volume which we have already noticed in this magazine. It contains four tables which have been compiled since that work was issued, and also a list of such errata as have been observed in it. The first table is an extremely useful one, being a table of corrections for reducing the numbers of Ångström and Cornu to the standard of Rowland's latest map. By means of these corrections all the lines tabulated in the previous volume can be reduced to absolute wave-lengths with great ease and accuracy.

Then follow two tables giving Liveing and Dewar's results for the spectra of cobalt and nickel. In each table there are two sets of numbers; one set, in italics, includes those lines whose wave-lengths have been directly measured by means of a grating, the other set, printed in ordinary type, gives the remaining lines. The author states on the first page that the scale used was that of Ångström; presumably, however, the remark applies only to the latter set of observations, the numbers in italics being already corrected and reduced to absolute wave-lengths.

Several lines in the cobalt spectrum are marked as being coincident with nickel lines and *vice versa*. The lines of wave-lengths 3452.9 and 3445.7 belonging to cobalt are marked as nickel lines; in the nickel spectrum they are not marked as cobalt lines, whereas an intermediate one, 3452.3, is so designated, although not to be found in the cobalt spectrum.

The greater portion of the book is taken up with the table giving Hasselberg's measurements of the lines found in the absorption-spectrum of iodine. The list includes over 3000 lines, 83 of which coincide with solar lines, and thus lead us to infer that iodine exists in the sun's atmosphere. The spectrum is interesting inasmuch as it contains a large number of double lines, and no fewer than 19 triple lines.

JAMES L. HOWARD.

*Star Groups. By J. ELLARD GORE, F.R.A.S.*  
(Crosby Lockwood and Son.)

THOSE who are acquainted with Mr. Gore's previous writings in the attractive realm of Sidereal Astronomy will gladly welcome this new contribution to the subject. The book consists of a series

of thirty carefully prepared maps of the principal Star Groups, and accompanying each one, on the opposite page, a short description is given of the most interesting objects. We should have liked to see these descriptions more complete, as there is considerable blank space left, and Mr. Gore is so much at home amongst stellar objects that he might readily have utilized it with further valuable references. The maps will prove of great utility to everyone who employs them as a means of becoming acquainted with the configuration of the leading Star Groups. Mr. Gore mentions in his preface that his "little maps are intended as an aid to the beginner," and this intention will doubtless be realized in many cases; but we hope the student will not feel nonplussed by the opening paragraph accompanying Map XIII., where it is stated: "Aries, the Ram, is the first sign of the Zodiac, or that in which the Vernal equinoctial point was situated in the time of Hipparchus. Owing, however, to the precession of the equinoxes this point has now retrograded into Pisces." Of course this reads simple enough to those well versed in the subject, but it is likely to prove too technical for mere beginners. On the whole, however, Mr. Gore's book undoubtedly merits commendation. Many a tyro can spend an agreeable hour in comparing the charts with the stars seen in the heavens and identifying the various groups as well as their individual stars. The volume is an example of Mr. Gore's well-known accuracy. We hope that, if a second edition is called for, the author will include one or two maps of Draco, a constellation which abounds in bright stars and which, large and straggling though it is, contains many interesting objects always visible in our latitude. The conspicuous stars in the head of Draco may be said to form a constellation by themselves; then there are  $\zeta$ ,  $\eta$ ,  $\theta$ , and  $\iota$ , which make up another bright group; a third attracts the eye near  $\delta$ ; and  $\phi$ ,  $\chi$ , and  $\psi$  form a pretty triangle about  $5^\circ$  N. of the pole of the ecliptic.

*An Elementary Treatise on the Integral Calculus, containing Applications to Plane Curves and Surfaces, and also a Chapter on the Calculus of Variations, with numerous Examples.* By B. WILLIAMSON, D. Sc., F.R.S. London: Longmans, 1891 (pp. xvi+463).

THE fact that this is the *Sixth* edition shows most unmistakably that Dr. Williamson has met the wants of students of the 'Calculus.' In the April No., 1881, we noticed the third edition. We have before us the first edition (a very modest volume), 1875 (pp. vi+267); the second edition, 1877 (pp. xi+348); the third edition, 1880 (pp. xiv+375). The issue of Six editions of a Mathematical treatise in sixteen years must be almost, if not quite, unprecedented. It is evident from the data above enumerated that the author is not content to rest upon his oars, but has laboured to make each edition better than its predecessor. A particular examination of so familiar a text-book is not called for here, and we shall simply



indicate wherein this edition differs from that previously noticed. The third edition closed with chapter xi. on Mean Value and Probability, this is now chapter xii., chapter xi. being devoted to Multiple Integrals (including an account of Dirichlet's Theorem, Green's Theorems, and applications to Spherical Harmonics). Chapter xiii. is on Fourier's Theorem. The novelties of this last edition are the two concluding chapters. Chapter xiv. treats of Line and Surface Integrals (discussing the theorems named after Stokes and Neumann): it is a short one and takes up pp. 401-412, concluding with a modification of Sir W. Thomson's theorem on the distribution of electricity on spherical conductors. In chapter xiv. Dr. Williamson gives an account (pp. 413-446) of the application of the Calculus of Variations to the determination of Curves possessing maxima and minima properties.

Students who require a further development than is given here are referred to the writings of Jellett, Carll, and Moigno. The work is supplemented by a large collection of Exercises and a sufficient Index. We can only hope that the author's labours may meet in the future with a success equal that which they have already attained.

*Solutions of Examples in Conic Sections, treated Geometrically.* By W. H. BESANT, *Sc.D., F.R.S.* London: George Bell, 1890.

WE have recently received this copy. As the book is in a third edition, it has evidently met a want. To our cost we know that we have spent many "ten minutes" in the unravelling of the Geometrical "Conundrums" contained in the author's "Conics." It is now interesting to compare our solutions with those before us, which though generally very concise furnish the student with a closely fitting Key to all the Problems. The book is most acceptable, but we trust that junior students will not have recourse to it until they have done their best in attempting to solve the Exercises themselves. A subsequent comparison of their own work with that of this "companion" volume will do them much good.

#### XIV. *Proceedings of Learned Societies.*

##### GEOLOGICAL SOCIETY.

[Continued from vol. xxxii. p. 230.]

November 11, 1891.—Sir Archibald Geikie, D.Sc., LL.D., F.R.S., President, in the Chair.

THE following communications were read:—

1. "On *Dacrytherium ovium* from the Isle of Wight and Quercy." By R. Lyddeker, Esq., B.A., F.G.S.
2. "Supplementary Remarks on Glen Roy." By T. F. Jamieson, Esq., F.G.S.

The author discusses the conditions that preceded the formation of the Glen Roy Lake, and appeals to a rain-map of Scotland in

support of his contention that the main snow-fall in Glacial times would be on the western mountains. He gives reasons for supposing that, previously to the formation of the lake, the valleys of the Lochaber lakes were occupied by ice, and that the period of the formation of the lakes was that of the decay of the last Ice-sheet.

He supports the correctness of the mapping of the terraces by the officers of the Ordnance Survey, and shows how the absence of the two upper terraces in Glen Spean and of the highest terrace in Glen Glaster simplifies the explanation of the formation of the lakes by ice-barriers.

The alluvium of Bohuntine is considered to be the gravel and mud that fell into the lake from the front of the ice when it stood at the mouth of Glen Roy during the formation of the two upper lines.

During the last stage of the lake, the ice in the valley of the Caledonian Canal is believed to have constituted the main barrier, whilst the Corry N'Eoin glacier played only a subordinate part.

The author suggests the possibility of a *débâcle* during the drop of water from the level of the highest to that of the middle terrace; and in support of this calls attention to the breaking down of the moraines of the Treig glacier at the mouth of the Rough Burn. He believes that when the water dropped to the level of the lowest terrace, it drained away quietly, at any rate until it receded from Upper Glen Roy.

In discussing Nicol's objections, he maintains that notches would not be cut at the level of the *cols*, and observes that the discrepancy between the heights of the terraces and those of the *cols* has probably been increased by the growth of peat over most of the ground about the watersheds.

The horizontality of the terraces is stated to be a fact, and cases are given where waterworn pebbles are found in connexion with the "roads," these being especially noticeable in places where the south-west winds would fully exert their influence, and the structure of the terraces is considered to be such as would be produced at the margins of ice-dammed lakes. Further information is supplied concerning the distribution of the boulders of Glen Spean syenite. These are found on the north side of the Spean Valley at the height of 2000 feet above the sea and 1400 feet above the river, and fragments of the syenite have been carried towards the north-east, north, and north-west.

In an Appendix, the author discusses Prof. Prestwich's remarks on the deltas, and his theory of the formation of the terraces.

November 25.—Sir Archibald Geikie, D.Sc., LL.D., F.R.S.,  
President, in the Chair.

The following communications were read:—

1. "On the Os pubis of *Polacanthus Foxi*." By Prof. H. G. Seeley, F.R.S., F.G.S.

2. "A Comparison of the Red Rocks of the South Devon Coast with those of the Midland and Western Counties." By Prof. Edward Hull, LL.D., F.R.S., F.G.S.

The author believes, with Dr. Irving, that the Red Rocks of Devonshire are representatives of the Permian and Trias which occupy so large a portion of the district bordering Wales and Salop and which extend into the Midland Counties, and comments on the remarkable resemblance between the representative beds on either side of the dividing ridge of Palæozoic rocks which underlies East Anglia and emerges beneath the Jurassic strata in Somersetshire.

He believes that the breccia forming the base of the series in the Torquay district is a representative of the Lower Permian division, but differs from Dr. Irving in assigning the red sandstones and marls of Exmouth to the Trias, and not to the Permian as that author has done. He compares them with the Lower Red and Mottled Sandstones, and regards the Marls as of local origin, thus causing the beds to diverge from the normal type.

The Budleigh Salterton Pebble-beds, with overlying sandstones and pebbly beds, he assigns to the horizon of the Pebble-beds of the Midland area, and points out that fossils of Silurian and Devonian types occur in the pebbles of both areas.

The Upper Division of the Bunter is well shown at Sidmouth, and the author takes a calcareous breccia, two feet thick, which is found in the cliffs, as the basement-bed of the Keuper division.

3. "Supplementary Note to the Paper on the 'Red Rocks of the Devon Coast-section,' Q. J. G. S. 1888." By the Rev. A. Irving, D.Sc., B.A., F.G.S.

In this note the author accepts Prof. Hull's determination (see above) of the breccia at Sidmouth as the base of the Keuper, and discusses the age of the sandstones containing vertebrate remains discovered by Messrs. Whitaker, Metcalfe, and Johnston-Lavis. He brings forward evidence in support of his view that these are really of Upper Bunter age, notwithstanding the character of the organisms.

He adds new material in support of his contention that the sandstones and marls which Prof. Hull assigns to the Lower Bunter are really Permian; but he is inclined to think that the breccias (in part, at least) pass laterally into the sandstones, and do not underlie them.

From this it follows that the break between the Permian and Trias of Devon is marked by the absence of the Lower Bunter of the Midlands, and the author quotes remarks of Mr. Usher in support of his view that there is an unconformity at the base of the Pebble-bed.

In conclusion the author refers to the difficulties of ascertaining the exact age of the breccias, and notes that we cannot prove that the highest Carboniferous beds are present in Devonshire. He observes that there is no valid reason why the great breccia-sandstone series of Devon should not be the true equivalent of the Lower Rothliegendes both in time and position in the sequence, and that some portions of them may be even older than the Rothliegendes of some

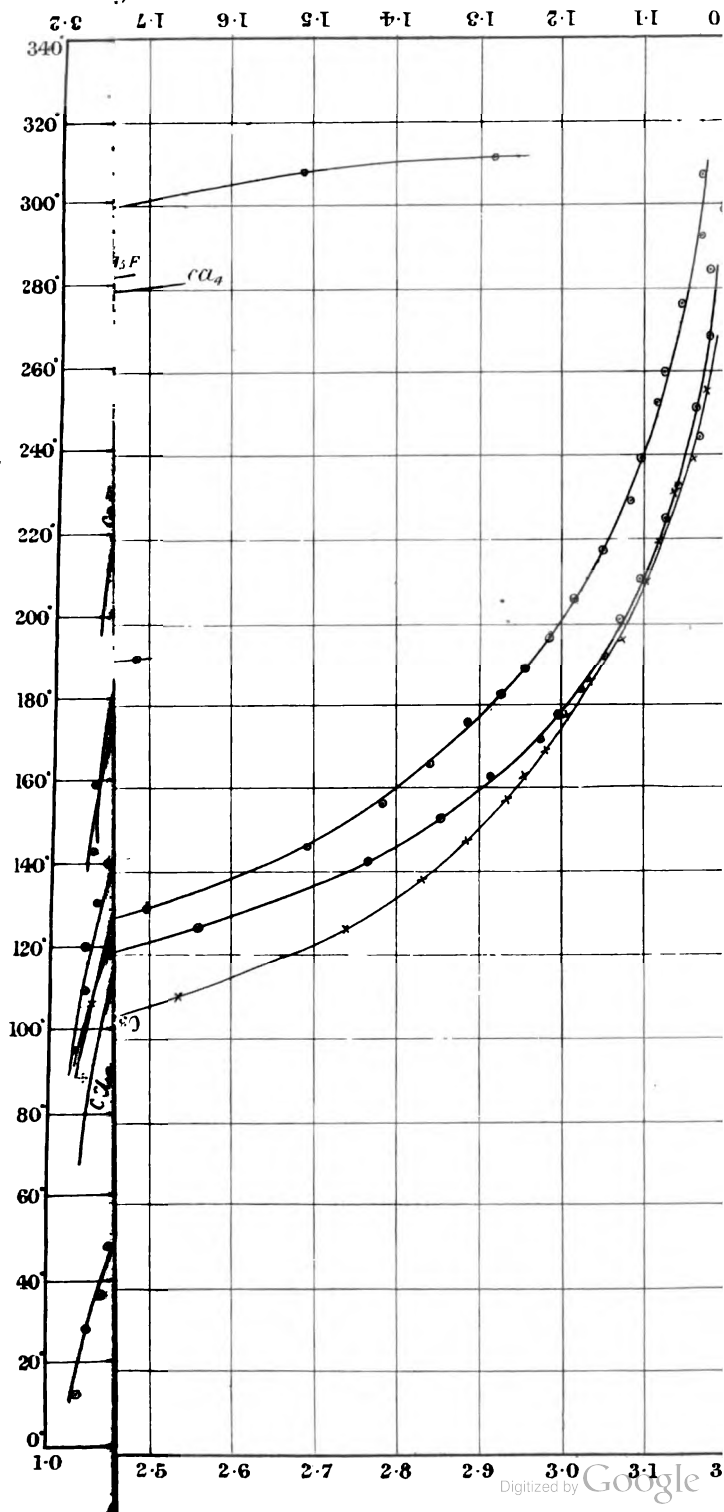
districts. He discusses the evidence furnished by the igneous rocks, and points out the abnormal position both for the British and German areas which these would occupy, if the breccias were of Triassic age.

### *XV. Intelligence and Miscellaneous Articles.*

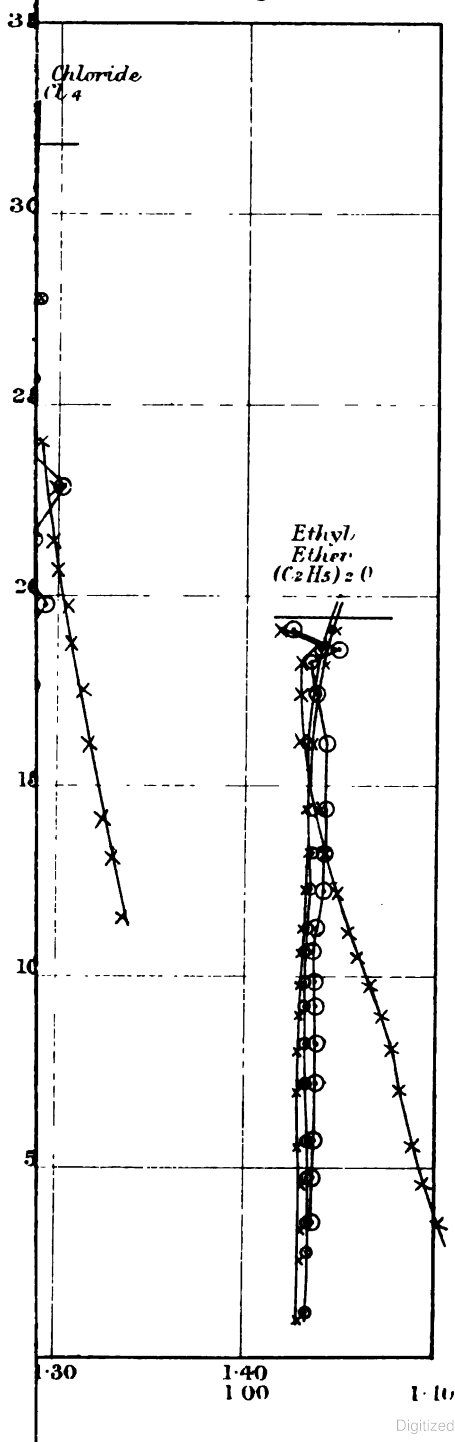
ON THE CONCORDANCE OF ORTHOBARIC CURVES FOR SOLUTIONS AND HOMOGENEOUS LIQUIDS. BY L. NATANSON.

PROF. Orme Masson, pursuing the line of inquiry started by M. van't Hoff with such success, has been able to point out a remarkable analogy between the systems formed by a liquid and a saturated vapour, with certain solutions partially soluble in each other. In order to put this analogy in its simplest form, let us assume that vapours are solutions of matter in a vacuum, and liquids solutions of vacuum in matter; the case of two mutual solutions in equilibrium will then become the general case, which will comprise, as a particular case, the ordinary equilibrium of a liquid in the presence of a saturated vapour.

From this point of view the author inquires whether it is not possible to transfer to solutions the well-known propositions of van der Waals on the fundamental relations which apply to various bodies in the state of saturated vapour. For this purpose he has constructed five "orthobaric lines," to use the expression of Ramsay and Young—that is to say, curves which show the relation of the volumes of the liquid and of the vapour with the temperature, even at the limits of saturation. The five combinations of liquids which have been chosen are those whose solubility has been investigated by M. Alexejeff, and the thermal expansion of which may be considered as known. These five combinations are as follows:—aniline and water, aniline and sulphur, isobutylic alcohol and water, phenol and water, essence of mustard and water. The consideration of these curves gave the values of the critical elements, that is to say the temperature and the volume of unit mass at the critical point of the solution. These values were then adopted as new units; and it was found that orthobaric curves referred to the respective critical elements agree with each other, the differences peculiar to them having disappeared. To this result another is attached. The orthobaric curve, which is unique for different solutions, is the same as that which applies to homogeneous bodies. This conclusion is corroborated by the calculation of orthobaric curves for ether, from Ramsay and Young and M. Battelli; for methylic alcohol and ethylic alcohol, from Ramsay and Young; lastly for carbonic acid and nitrogen protoxide, from MM. Cailletet and Mathias; as well as by the detailed comparison of all those curves with those which have been calculated for solutions.—*Bulletin de l'Académie des Sciences de Cracovie*, June 1891. (*Communicated by the Author.*)

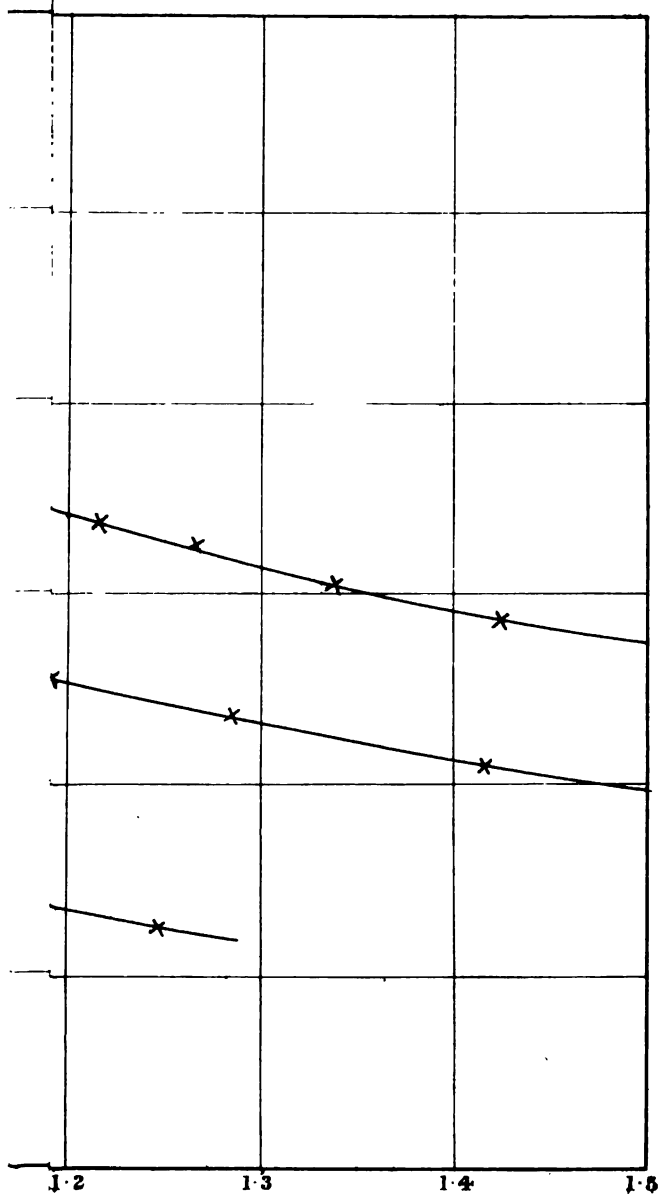
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IV. On the Connexion between Recurring Formulæ involving Sums of Divisors and the Corresponding Formulæ involving Differences between Sums of Even and Uneven Divisors. By J. W. L. GLAISHER, Sc.D., F.R.S. ....	54
V. On the Calculation of the Induction-Coefficients of Coils, and the Construction of Standards of Inductance, and on Absolute Electrodynamometers. By ANDREW GRAY, M.A., Professor of Physics in the University College of North Wales .....	62
VI. The Influence of Flaws and Air-cavities on the Strength of Materials. By J. LAZMOR, M.A., Fellow of St. John's College, Cambridge .....	70
VII. A Galvanometric Method of Measuring H. By R. A. LEHFELDT, B.A., B.Sc., Demonstrator at Firth College, Sheffield...	78
VIII. On the Theory of Electrolytic Conduction of Clausius; and on some recent Evidence for the Dissociation Theory of Electrolysis. By J. BROWN.....	82
IX. On a New Method for obtaining a Constant Temperature. By Mr. HENRY CREW, Instructor in Physics in Haverford College .	89
X. On the Existence of a Compound of Gold and Tin. By A. P. LAURIE, M.A.....	94
XI. The Variation in the Density of Water with the Temperature. By D. MENDELÉEFF .....	99
XII. The Densities of Sulphuric-Acid Solutions. By SPENCER UMFREVILLE PICKERING, F.R.S. ....	132
XIII. Notices respecting New Books:—Prof. OSTWALD's 'Solutions;' being the Fourth Part of a Text-Book of General Chemistry; Dr. WATTS's Index of Spectra, Appendix B; Mr. GORE's Star Groups; Dr. WILLIAMSON's Elementary Treatise on the Integral Calculus; Dr. BESANT's Solutions of Examples in Conic Sections .....	144–149
XIV. Proceedings of Learned Societies:— GEOLOGICAL SOCIETY .....	149–151
XV. Intelligence and Miscellaneous Articles:— On the Concordance of Orthobaric Curves for Solutions and Homogeneous Liquids, by L. NATANSON .....	152

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# PHILOSOPHICAL MAGAZINE

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[FIFTH SERIES.]

FEBRUARY 1892.

XVI. *On the Generalizations of Van der Waals regarding "Corresponding" Temperatures, Pressures, and Volumes.*  
By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol\*.

[Plates I.-III.]

IN his dissertation *Die Continuität des gasförmigen und flüssigen Zustandes* (Roth's translation, Leipzig, 1881, p. 128) Van der Waals has deduced the following generalizations from his fundamental equation

$$\left(p + \frac{a}{v^2}\right)(v-b) = R(1+at).$$

If the absolute temperatures of various substances be proportional to their absolute critical temperatures, their vapour-pressures will be proportional to their critical pressures, and their volumes, both as liquid and as saturated vapour, will be proportional to their critical volumes.

At the time, however, that Van der Waals's great work was published, the available experimental data were insufficient to satisfactorily test the accuracy of these generalizations.

Since then the conclusions of Van der Waals have been subjected to a large amount of criticism, both adverse and favourable; and while it is now generally recognized that the relations between the temperatures, pressures, and volumes of liquids and gases cannot be represented by so simple a formula as that quoted above, it has nevertheless been accepted as correct by some authors, who have made it the basis of further generalizations.

And although the general verdict with regard to the strict accuracy of the formula itself can hardly be considered

\* Communicated by the Physical Society: read November 6, 1891.

*Phil. Mag.* S. 5. Vol. 33. No. 201. Feb. 1892.

favourable, the notion of "corresponding" states has received wide acceptance; and, indeed, the generalizations regarding corresponding temperatures, pressures, and volumes might still be true even though the formula on which they were originally based required some alteration.

In order to study the relations, for instance, between the specific volumes of different substances, determinations were made in the first place at the same temperature, generally at 0° C.; later on it was considered that the conditions would be more uniform if the comparison were made at the boiling-points of the substances under normal atmospheric pressure. It is now, however, usually admitted that in order to obtain the best results the volumes should be determined at "corresponding" temperatures—that is to say, at absolute temperatures proportional to the absolute critical temperatures of the various bodies—or at their boiling-points under corresponding pressures—the two methods of comparison being, according to Van der Waals, identical.

During the last four years I have been engaged in a research on the vapour-pressures and specific volumes—both in the liquid state and as saturated vapour—of the following substances:—benzene, fluorbenzene, chlorobenzene, bromobenzene, iodobenzene\*, carbon tetrachloride and stannic chloride†; the vapour-pressures and specific volumes of methyl‡, ethyl§, and propyl alcohols||, and of ethyl ether¶ have also been determined by Dr. Ramsay and myself. We obtained the same constants for acetic acid\*\* up to 280°; and I have recently extended the observations with this substance up to the critical point (*ibid.* lix. p. 903).

The methods employed for the determination of the vapour-pressures of benzene and its halogen derivatives and for the specific volumes of these bodies in the liquid state were, with slight modifications, the same as those made use of by Ramsay and myself in our researches on the alcohols and ether.

Carbon tetrachloride, however, acts on mercury at high temperatures, and stannic chloride renders it unfit for use—though the chemical action is very slight—even at low temperatures; a considerable alteration in the method of determining vapour-pressures was therefore made (*Trans. Chem. Soc.* lix. p. 917).

For the determination of the specific volumes of stannic chloride in the liquid state and of all the substances in the condition of saturated vapour an entirely different method was

\* *Trans. Chem. Soc.* lv. p. 486, and lix. p. 125. † *Ibid.* lix. p. 911.

‡ *Phil. Trans.* clxxviii. A, p. 313.

§ *Ibid.* 1886, part i. p. 123.

|| *Ibid.* clxxx. p. 137.

¶ *Ibid.* clxxviii. A, p. 57.

\*\* *Trans. Chem. Soc.* xlix. p. 790.



employed, and this has been fully described in the *Trans. Chem. Soc.* 1891, p. 37. This method is applicable to substances that attack mercury, and from the data it affords the specific volumes both of liquid and saturated vapour may be calculated; it is also available at any temperature up to the critical point. A modification of the method is described in the *Trans. Chem. Soc.* lix. p. 929.

The object of this paper is to show how far the generalizations of Van der Waals have been verified by the experimental results.

If all the relations were strictly true, it would obviously make no difference whether the specific (or molecular) volumes were compared at corresponding temperatures or corresponding pressures; but it may be stated at once that it is only in a limited number of cases that, when the absolute temperatures are proportional to the absolute critical temperatures, the vapour-pressures are also proportional to the critical pressures. It is therefore necessary to compare the various substances, not only at corresponding temperatures but also at corresponding pressures. The best mode of procedure would probably be to give the temperatures, pressures, and volumes of each substance in terms of the critical constants of that body; but the critical volumes of only a few of the compounds have been directly determined, and it has therefore been necessary to compare the various substances with one of them taken as a standard. The very simple relations observed between the four monohalogen derivatives of benzene (*Trans. Chem. Soc.* 1889, p. 486), and the fact that the constants of fluorobenzene have been determined up to the critical point, render that substance the most suitable for the purpose.

The experimental data and the ratios calculated from them are given in the following tables.

- I. Critical constants—temperature, pressure, volume.
- II. Corresponding pressures.
- III. Corresponding temperatures.
- IV. Boiling-points on absolute scale at corresponding pressures.
- V. Vapour-pressures at corresponding temperatures.
- VI. Molecular volumes of liquids at corresponding pressures.
- VII. Molecular volumes of liquids at corresponding temperatures.
- VIII. Molecular volumes of saturated vapour at corresponding pressures.
- IX. Molecular volumes of saturated vapour at corresponding temperatures.
- X. Ratios of absolute temperatures to those of fluorobenzene at corresponding pressures.

XI. Ratios of vapour-pressures at corresponding temperatures.

XII. Ratios of molecular volumes of liquid at corresponding pressures.

XIII. Ratios of molecular volumes of liquid at corresponding temperatures.

XIV. Ratios of molecular volumes of saturated vapour at corresponding pressures.

XV. Ratios of molecular volumes of saturated vapour at corresponding temperatures.

In calculating the molecular volumes the following molecular weights have been employed :—

$C_6H_5F$ ... 95.8	$C_6H_5I$ ... 203.4	$SnCl_4$ ..... 259.3	$C_2H_5OH$ ... 45.90
$C_6H_5Cl$ ... 112.2	$C_6H_6$ ... 77.84	$(C_2H_5)_2O$ ... 73.84	$C_3H_7OH$ ... 59.87
$C_6H_5Br$ ... 156.6	$CCl_4$ ... 153.45	$CH_3OH$ ... 31.93	$CH_3COOH$ 59.86

TABLE I.—Critical Constants.

Substance.	Formula.	Temperature.		Pressure, in millim.	Volume, in c.c.	
		Centi- grade.	Absolute.		of a gram.	Molecular.
Fluorbenzene.....	$C_6H_5F$ .	236.55	559.55	33912	2.43	233
Chlorobenzene .....	$C_6H_5Cl$ .	(360)	(633)	(33912)	(2.34)	(262)
Bromobenzene .....	$C_6H_5Br$ .	(397)	(670)	(33912)	(1.76)	(275)
Iodobenzene .....	$C_6H_5I$ .	(448)	(721)	(33912)	(1.47)	(298)
Benzene .....	$C_6H_6$ .	288.5	561.5	36395	2.82	219
Carbon tetrachloride	$CCl_4$ .	283.15	556.15	34180		
Stannic Chloride ...	$SnCl_4$ .	318.7	591.7	28080		
Ether .....	$(C_2H_5)_2O$ .	194.4	467.4	27060		
Methyl Alcohol.....	$CH_3OH$ .	240.0	513.0	59760		
Ethyl Alcohol .....	$C_2H_5OH$ .	243.1	516.1	47850		
Propyl Alcohol .....	$C_3H_7OH$ .	263.7	536.7	38120		
Acetic Acid .....	$CH_3COOH$ .	321.6	594.6	43400	2.46	147

The brackets indicate calculated values. In the case of chlorobenzene, bromobenzene, and iodobenzene the critical temperatures and volumes given depend on the assumption that the critical pressures are equal. The critical constants of chlorobenzene have been observed, but the determinations could not be made with the same degree of accuracy as those of fluorobenzene, and the calculated values have therefore been adopted in this paper. The observed values are :—temperature, 359.2 to 359.45; pressure, 33926 to 33998 millim.; molecular volume, 262 to 275 cubic centim. The temperatures given in the original paper (Trans. Chem. Soc. lv. p. 518) are 360.55–360.8; but the boiling-point of mercury, the vapour of which was employed as a jacket, has since been shown to be lower than was at that time adopted.

TABLE II.  
Corresponding Pressures.

Halogen Derivatives of Benzene.	C <sub>6</sub> H <sub>6</sub> .	CCl <sub>4</sub> .	SnCl <sub>4</sub> .	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	CH <sub>3</sub> OH.	C <sub>2</sub> H <sub>5</sub> OH.	O <sub>3</sub> H <sub>7</sub> OH.	CH <sub>3</sub> COOH.
20	21.46	20.16	16.56	15.96	35.24	28.22	22.48	25.60
50	53.66	50.40	41.40	39.90	88.11	70.55	56.21	63.99
100	107.3	100.8	82.24	79.80	176.2	141.1	112.4	128.0
200	214.6	201.6	165.6	159.6	352.4	282.2	224.8	256.0
400	429.3	403.2	331.2	319.2	704.9	564.4	449.7	511.9
760	815.6	766.0	620.4	606.5	1339	1072	854.3	972.6
1000	1078.0	1008	822.4	798.0	1762	1411	1124	1280
1500	1610	1512	1242	1197	2643	2116	1686	1920
2000	2146	2016	1656	1596	3524	2822	2248	2560
3000	3220	3023	2484	2394	5287	4233	3372	3839
4000	4293	4032	3312	3192	7049	5644	4497	5119
5000	5366	5040	4140	3990	8811	7055	5621	6399
6000	6439	6048	4920	4787	10673	8467	6745	7679
7000	7513	7055	5796	5586	12337	9876	7869	8959
8000	8586	8063	6624	6384	14096	11288	8963	10238
10000	10732	10079	8224	7980	17624	14109	11241	12798
12000	12879	12096	9696	9376	21145	16932	13490	15357
14000	14998	14118	12419	11970	26430	21164	16962	19197
20000	21464	20156	16562	15962	35245	28223	22480	25586
25000	26831	25200	20701	19948	44055	35278	28100	31995
28000	30047	28223	23185	22341	49340	39509	31477	35834
30000	32197	30234	24843	23939	52869	42825	33721	38394
32000	34340	32255	26497	25533	56390	46154	35975	40963
33012	36395	34182	28080	27060	59760	47890	38120	43400

TABLE III.  
Corresponding Temperatures (absolute).

Pressure $C_6H_6F.$	$C_6H_6F.$	$C_6H_5Ol.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$CCl_4.$	$SnCl_4.$	$(O_2H_2)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
20	272.25	308.0	326.0	350.8	273.2	270.6	287.9	227.4	249.6	251.1	261.15	289.3
50	289.3	327.3	346.4	372.8	290.3	287.55	305.9	241.65	285.25	286.85	277.5	307.4
100	303.9	343.8	363.9	391.6	304.65	302.05	321.35	253.85	278.6	280.3	291.5	322.95
200	320.25	362.3	383.45	413.65	321.35	318.3	338.65	267.5	293.6	295.4	307.15	340.3
400	338.75	383.2	405.6	436.5	339.95	336.7	358.2	289.95	310.55	312.45	324.9	359.95
760	358.1	405.1	428.8	461.4	359.35	355.9	378.65	299.15	328.3	330.3	343.45	390.5
1000	367.3	415.5	439.8	473.3	368.6	365.05	388.4	306.8	336.75	338.75	352.3	390.3
1500	382.0	432.15	457.4	492.2	383.35	379.65	403.95	319.1	350.2	352.95	366.4	405.9
2000	393.25	444.85	470.85	506.7	394.6	390.85	415.85	328.5	360.55	362.7	377.2	417.9
3000	410.4	464.25	491.4	528.8	411.85	407.9	434.0	342.8	376.25	378.55	393.65	436.1
4000	423.8	479.4	507.45	546.1	425.3	421.2	448.15	354.0	388.55	390.9	406.5	450.35
5000	434.85	491.95	520.7	.....	436.35	432.2	459.85	363.25	398.7	401.1	417.1	462.1
6000	444.25	502.55	531.95	.....	445.8	441.55	469.8	371.1	407.3	409.75	426.1	472.1
7000	452.8	512.25	542.2	.....	454.4	450.15	478.8	378.25	415.15	417.65	434.3	481.15
8000	460.4	520.85	551.3	.....	462.0	457.6	486.85	384.6	422.1	424.65	441.6	489.25
10000	473.6	535.75	.....	.....	475.25	470.7	500.8	395.6	434.2	436.8	454.25	503.25
12000	484.95	548.6	.....	.....	486.65	482.0	512.8	405.1	444.6	447.3	465.15	515.3
15000	498.7	565.3	.....	.....	501.45	496.65	528.4	417.4	458.15	460.9	479.3	531.0
20000	519.7	587.9	.....	.....	521.5	516.55	549.55	434.1	476.45	479.35	498.45	552.25
25000	536.0	606.35	.....	.....	537.85	532.75	566.8	447.7	491.4	494.35	514.1	569.55
28000	544.5	615.95	.....	.....	546.4	541.2	575.8	454.85	499.2	502.2	522.25	578.6
30000	550.0	622.2	.....	.....	551.9	546.85	581.6	459.4	504.25	507.3	527.55	584.45
32000	555.0	627.85	.....	.....	556.95	551.6	586.9	463.6	506.85	511.9	532.3	589.75
33912	559.55	(633.0)	(670.0)	(721.0)	561.5	556.15	591.7	467.4	513.0	516.1	536.7	594.6

TABLE IV.  
Boiling-points on Absolute Scale at corresponding Pressures.

Pressure $C_2H_2F_4$	$O_2H_6F_4$	$C_2H_5Cl$	$C_2H_5Br$	$C_2H_5I$	$C_2H_6$	$CCl_4$	$SnCl_4$	$(O_2H_2)_2O$	$CH_3OH$	$C_2H_5OH$	$C_2H_5OH$	$CH_3COOH$
20	272.25	308.05	326.3	351.25	269.25	264.05	290.75	.....	275.7	286.7	299.4	307.05
50	289.3	327.1	346.3	372.75	286.25	281.05	308.65	.....	291.65	301.2	314.55	325.7
100	303.9	343.4	368.6	391.3	300.9	295.5	323.7	.....	304.85	314.05	327.45	341.5
200	320.25	361.95	383.05	412.2	317.15	311.9	341.0	.....	319.55	328.3	341.6	359.2
400	338.75	382.8	405.3	436.1	336.3	330.5	360.3	285.0	336.0	344.0	357.25	378.9
700	358.1	404.9	429.0	461.55	355.65	350.0	380.75	301.2	353.05	360.3	373.55	399.3
1000	367.3	415.4	440.05	473.5	364.95	359.25	390.05	308.7	361.0	367.75	381.25	408.9
1500	382.0	432.2	457.8	492.45	379.85	374.15	405.6	320.9	373.3	379.6	393.2	424.1
2000	393.25	445.0	471.3	507.0	391.3	385.7	417.35	330.2	381.6	388.7	402.25	435.8
3000	410.4	464.6	492.0	529.0	408.9	403.25	435.3	344.5	394.75	402.25	415.2	453.3
4000	423.8	479.9	507.95	545.65	422.5	416.8	449.2	355.55	407.6	412.7	425.95	468.6
5000	434.85	492.45	521.05	.....	433.75	428.05	460.8	364.5	416.5	421.2	435.7	477.5
6000	444.25	503.0	532.1	.....	443.5	437.75	470.3	372.4	424.0	428.5	443.26	486.7
7000	452.8	512.5	542.05	.....	452.15	446.3	479.6	379.2	430.7	435.0	449.95	494.8
8000	460.4	520.95	550.9	.....	459.8	454.15	487.35	385.35	436.7	440.95	456.0	502.05
10000	473.6	535.5	.....	.....	473.3	467.8	500.75	396.0	446.75	450.95	466.4	514.4
12000	484.95	548.2	.....	.....	485.0	479.5	518.05	405.25	455.5	459.8	475.6	525.05
15000	499.7	564.6	.....	.....	500.05	494.35	528.6	417.05	468.75	470.65	487.4	538.5
20000	519.7	587.25	.....	.....	520.5	515.0	549.5	433.6	481.25	485.75	503.6	557.0
25000	536.0	605.7	.....	.....	537.1	531.95	566.7	447.45	494.7	498.15	517.2	572.85
28000	544.5	615.25	.....	.....	546.05	540.85	575.85	454.7	501.45	504.5	524.4	580.5
30000	550.0	621.5	.....	.....	551.6	546.25	581.55	459.2	505.55	508.65	529.0	586.3
32000	555.0	627.2	.....	.....	556.75	551.5	586.75	463.45	509.35	512.55	533.15	590.2
33912	559.55	632.5	(670.0)	(721.0)	561.5	556.15	591.7	467.4	513.0	516.1	536.7	594.6

TABLE V.  
Vapour-pressures at corresponding Temperatures.

Temp. $C_6H_5F$ .	$C_6H_5F$ .	$C_6H_5Cl$ .	$C_6H_5Br$ .	$C_6H_5I$ .	$C_6H_6$ .	$COCl_2$ .	$SnCl_4$ .	$(C_2H_5)_2O$ .	$OH_2OH$ .	$C_2H_5OH$ .	$C_2H_5OH$ .	$CH_3COOH$ .
272.25	20	19.95	19.75	19.70	28.76	29.21	14.13	.....	.....	.....	.....	9.53
289.3	50	50.40	50.10	50.10	65.46	69.50	36.35	.....	17.96	.....	.....	24.77
303.9	100	101.7	101.2	101.0	128.8	184.6	74.13	.....	41.69	.....	.....	56.23
320.25	200	203.0	202.1	202.5	252.9	259.4	151.5	140.9	98.63	20.13	20.13	122.3
338.75	400	403.5	403.2	402.7	495.5	501.2	308.7	291.1	281.7	50.64	50.64	263.0
358.1	760	763.8	758.6	758.6	912.0	916.2	591.6	562.3	515.2	129.1	129.1	538.3
367.3	1000	1001	994.3	997.7	1183	1189	784.3	746.4	728.9	310.5	310.5	739.6
387.0	1500	1493	1491	1495	1766	1740	1191	1130	1211	452.9	452.9	1176
393.25	2000	1995	1982	1989	2325	2272	1598	1515	.....	790.7	790.7	1635
410.4	3000	2979	2965	2992	3432	3350	2415	2288	.....	1175	1175	2576
423.8	4000	3967	3967	4027	4545	4406	3240	3076	2897	2042	2042	3589
434.85	5000	4949	4972	.....	5636	5451	4064	3868	5559	3027	3027	4656
444.25	6000	5943	5977	.....	6722	6464	4881	4651	6988	4102	4102	5735
452.8	7000	6982	7015	.....	7834	7516	5715	5476	8521	5218	5218	6894
460.4	8000	7998	8054	.....	8913	8581	6589	6281	10070	6449	6449	8083
473.6	10000	10025	.....	.....	11079	10556	8252	7907	13351	7700	7700	10471
484.95	12000	12050	.....	.....	13228	12560	9897	9539	15351	10292	10292	13002
499.7	15000	15136	.....	.....	16425	15613	12402	12023	16788	13017	13017	16943
519.7	20000	20137	.....	.....	21752	20583	16558	16088	22284	17398	17398	23796
536.0	25000	25206	.....	.....	27071	25468	20725	20045	31659	25061	25061	30726
544.5	28000	28184	.....	.....	30200	28347	23174	22413	41543	39037	39037	39784
550.0	30000	30234	.....	.....	32322	30374	24960	23988	47479	37844	37844	39554
555.0	32000	32211	.....	.....	34435	32285	26516	25615	51761	41400	41400	39552
559.55	33912	(33012)	(33912)	(33912)	36395	34180	28080	27060	55947	44668	44668	40991
									59760	47850	47850	43400

TABLE VI.  
Molecular Volumes of Liquid at corresponding Pressures.

Pressure. $C_6H_5F$ .	$O_2H_5F$ .	$C_6H_5Cl$ .	$C_6H_5Br$ .	$C_6H_5I$ .	$C_6H_5$ .	$CCl_4$ .	$SnCl_4$ .	$(C_2H_5)_2O$ .	$CH_3OH$ .	$C_2H_5OH$ .	$C_3H_7OH$ .	$OH_3COOH$ .
20	91.47	102.89	107.99	116.79	86.10	.....	116.17	.....	.....	57.69	74.99	57.85
50	93.30	104.88	110.04	119.03	87.87	94.91	118.66	.....	40.27	58.66	76.19	59.00
100	94.92	106.63	111.89	121.09	89.41	96.58	120.78	.....	40.77	59.51	77.29	60.06
200	96.80	108.75	114.10	123.52	91.23	98.50	123.32	.....	41.56	60.51	78.56	61.33
400	99.06	111.32	116.81	126.48	93.51	100.86	126.51	102.21	42.43	61.72	80.06	62.85
760	101.59	114.26	119.94	129.86	95.91	103.52	129.80	104.94	43.42	63.11	81.81	64.59
1000	102.90	115.75	121.47	131.56	97.12	104.87	131.52	106.31	43.92	63.80	82.70	65.46
1500	105.10	118.23	124.11	134.40	99.20	107.19	134.47	108.60	44.76	64.97	84.20	66.91
2000	107.00	120.24	126.24	136.72	100.98	108.10	136.88	110.46	45.45	65.07	85.47	68.09
3000	110.03	123.69	129.86	140.63	103.89	112.23	140.88	115.49	46.60	67.65	87.65	70.01
4000	112.64	126.65	132.90	143.73	106.35	114.86	144.09	118.08	47.56	69.10	89.50	71.61
5000	114.98	129.27	135.68	.....	108.50	117.16	147.10	118.44	48.42	70.48	91.24	73.04
6000	117.06	131.72	138.23	.....	110.62	119.39	149.62	120.70	49.28	71.67	92.87	74.38
7000	119.14	134.08	140.75	.....	112.48	121.32	152.62	122.91	50.07	72.89	94.46	75.69
8000	121.19	136.83	143.18	.....	114.38	123.38	155.24	125.12	50.88	73.97	96.03	76.94
10000	125.04	140.72	.....	.....	117.96	127.39	160.27	129.33	52.36	76.15	99.01	79.37
12000	128.80	145.10	.....	.....	121.55	131.99	165.56	133.36	53.87	78.33	101.99	81.79
15000	134.64	.....	.....	.....	127.12	137.34	173.87	139.23	56.17	81.63	106.57	85.30
20000	145.08	.....	.....	.....	137.20	146.19	187.29	149.62	60.54	88.22	114.89	91.86
25000	158.40	.....	.....	.....	149.80	161.89	.....	164.15	66.10	96.34	125.67	100.1
28000	169.35	.....	.....	.....	160.20	173.55	.....	176.18	70.92	102.59	134.41	107.4
30000	179.40	.....	.....	.....	169.60	183.37	.....	186.52	75.04	109.10	142.52	113.4
32000	193.0	.....	.....	.....	182.3	196.26	.....	201.80	81.49	118.01	153.99	121.8
33912	233.0	.....	.....	.....	219.0	.....	.....	.....	.....	.....	.....	147.0

TABLE VII.  
Molecular Volumes of Liquid at corresponding Temperatures.

Temp. $C_2H_5F.$	$C_2H_5F.$	$C_2H_5Cl.$	$C_2H_5Br.$	$C_2H_5I.$	$C_2H_6.$	$CCl_4.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$O_2H_5OH.$	$O_3H_5OH.$	$CH_3COOH.$
272.25	91.47	102.88	107.95	116.73	86.50	.....	115.78	.....	.....	.....	.....	56.85
289.3	93.80	104.89	110.04	119.03	88.28	95.63	118.24	.....	.....	73.38	.....	57.87
303.9	94.92	106.69	111.93	121.12	89.86	97.33	120.45	.....	.....	74.39	.....	58.93
320.25	96.80	108.80	114.13	123.57	91.73	99.31	122.98	.....	40.36	75.59	.....	59.99
338.75	99.05	111.37	116.86	126.50	93.95	101.69	125.99	101.86	41.12	77.09	.....	61.38
356.1	101.69	114.17	119.93	129.85	96.38	104.36	129.47	104.60	42.01	78.71	.....	62.97
367.3	102.90	115.77	121.44	131.54	97.62	105.76	131.18	105.97	42.47	79.56	.....	63.81
382.0	105.10	118.21	124.06	134.36	99.73	108.08	134.13	108.26	43.25	81.02	.....	65.19
393.25	107.00	120.22	126.17	136.67	101.48	109.99	136.55	110.10	43.69	82.22	.....	66.30
410.4	110.03	123.63	129.76	140.59	104.41	113.11	140.57	113.10	44.97	84.29	.....	68.12
433.8	112.64	126.56	132.79	144.05	106.90	115.73	143.83	115.72	45.92	86.23	.....	69.67
434.85	114.98	129.17	135.60	.....	109.04	118.03	146.87	118.11	46.77	87.80	.....	71.06
444.25	117.06	131.60	138.18	.....	111.05	120.15	149.07	120.32	47.54	89.43	.....	73.32
452.8	119.14	134.05	140.77	.....	113.05	122.28	152.39	122.61	48.29	91.00	.....	75.56
460.4	121.19	136.33	143.30	.....	114.90	124.31	155.09	124.86	49.06	92.50	.....	77.16
473.6	125.04	140.79	.....	.....	118.51	128.32	160.32	129.18	50.53	95.61	.....	79.57
484.95	128.80	145.29	.....	.....	122.07	132.28	165.43	133.24	52.03	98.67	.....	83.31
499.7	134.64	.....	.....	.....	127.68	138.29	173.24	139.02	54.36	103.37	.....	89.00
519.7	145.08	.....	.....	.....	137.81	149.16	187.94	150.26	58.72	111.87	.....	99.25
536.0	158.40	180.0	.....	.....	150.60	162.81	.....	164.37	64.31	122.55	.....	106.45
544.5	169.35	192.4	.....	.....	160.70	174.09	.....	176.48	69.13	125.55	.....	112.15
550.0	179.40	204.0	.....	.....	170.00	184.06	.....	187.11	73.63	130.50	.....	120.8
555.0	183.0	222.4	.....	.....	183.00	196.57	.....	202.32	80.43	150.87	.....	147
559.56	233.0	.....	.....	.....	219.0	.....	.....	.....	.....	.....	.....	.....

Approximate.



TABLE VIII.  
Molecular Volumes of Saturated Vapour at corresponding Pressures.

Pressure $C_6H_6F$	$C_6H_6F$	$C_6H_5Cl$	$C_6H_5Br$	$C_6H_5I$	$C_6H_6$	$CCl_4$	$SnCl_4$	$(C_2H_5)_2O$	$CH_3OH$	$C_2H_5OH$	$C_2H_5OH$	$CH_3COOH$
20	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	891000
50	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	178000
100	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	93700
200	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	50750
400	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	27410
760	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	16400
22000	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	12010
1000	22000	24650	25750	27950	20400	21150	28150	22800	11740	15550	18890	8275
1500	15000	16900	17600	19200	13900	14550	19100	15550	7945	10500	13410	6340
2000	11400	12900	13400	14600	10830	11120	14540	11780	5987	7980	10120	4341
3070	7680	8760	9180	9900	7235	7550	9840	7370	4032	5354	6760	3906
4000	5785	6615	6910	7465	5500	5740	7445	6005	3022	4024	5056	2673
5000	4634	5308	5544	.....	4421	4618	5943	4811	2410	3218	4041	2244
6000	3857	4411	4624	.....	3694	3864	4985	4005	1995	2672	3335	1927
7000	3288	3771	3954	.....	3167	3282	4232	3420	1698	2275	2861	1686
8000	2871	3251	3445	.....	2759	2864	3998	2976	1474	1974	2486	1349
10000	2285	2576	.....	.....	2175	2257	2948	2358	1158	1558	1961	1116
12000	1862	2108	.....	.....	1771	1851	2388	1936	943	1256	1568	879
15000	1447	.....	.....	.....	1371	1440	1841	1508	728	982	1239	628
20000	1009	.....	.....	.....	958	1012	1274	1052	499	651	837	457
25000	733	.....	.....	.....	689	738	.....	759	352	468	594	374
28000	601	.....	.....	.....	563	597	.....	622	283	396	489	325
30000	516	.....	.....	.....	489	519	.....	542	245	332	426	275
32000	440	.....	.....	.....	.....	447	.....	454	208	276	368	147
33912	233	.....	.....	.....	219	.....	.....	.....	.....	.....	.....	.....

TABLE IX.

Molecular Volumes of Saturated Vapour at corresponding Temperatures.

Temp. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_5.$	$OCl_4.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$C_3H_7OH.$	$CH_3COOH.$
272.25	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	384500
289.3	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	198500
303.9	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	99700
320.25	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	49500
338.75	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	26150
358.1	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	19850
367.3	22000	24650	25850	28000	18550	18250	38350	31650	38000	45700	.....	33800
382.0	15000	16920	17770	19280	12780	12760	29400	24250	27400	27050	.....	12940
393.25	11400	12830	13540	14710	9865	9865	15060	16400	16850	18600	.....	9625
410.4	7680	8830	9225	9930	6900	6870	10100	12400	11950	10850	.....	6280
423.8	5785	6653	6968	7413	5164	5268	7595	8320	7260	7430	.....	4613
434.85	4634	5353	5576	.....	4198	4281	6060	4972	5065	5521	.....	3622
444.25	3857	4457	4645	.....	3544	3597	5035	4116	3628	4345	.....	2968
452.8	3298	3780	3954	.....	3023	3083	4285	3491	2489	3532	.....	2495
460.4	2871	3281	3414	.....	2649	2692	3733	3027	2094	2951	.....	2198
473.6	2265	2567	.....	.....	2099	2150	2944	2374	1560	2178	.....	1652
484.95	1802	2077	.....	.....	1734	1776	2404	1939	1219	1690	.....	1326
499.7	1447	.....	.....	.....	1340	1398	1845	1605	890	1218	.....	1005
519.7	1009	.....	.....	.....	934	986	1274	1040	578	770	.....	687
536.0	733	.....	.....	.....	677	719	.....	753	389	516	.....	487
544.5	601	.....	.....	.....	569	592	.....	619	305	415	.....	393
550.0	516	.....	.....	.....	485	514	.....	538	257	349	.....	335
555.0	440	.....	.....	.....	.....	446	.....	451	213	285	.....	281
559.55	233	.....	.....	.....	219	.....	.....	.....	.....	.....	.....	147

TABLE X.  
Ratios of Absolute Temperatures (Boiling-Points) to those of Fluorobenzene at corresponding Pressures.

Pressure $C_6H_5F$ .	$C_6H_5F$ .	$C_6H_5Ol$ .	$C_6H_5Br$ .	$C_6H_5I$ .	$C_6H_6$ .	$CCl_4$ .	$SnCl_4$ .	$(C_2H_5)_2O$ .	$OH_2OH$ .	$C_2H_5OH$ .	$C_3H_7OH$ .	$OH_3COOH$ .
20	1.0000	1.1315	1.1985	1.2802	.9890	.9899	1.0679	.....	1.0127	1.0494	1.0997	1.1278
50	"	1.1307	1.1970	1.2885	.9895	.9715	1.0669	.....	1.0081	1.0411	1.0873	1.1258
100	"	1.1300	1.1964	1.2876	.9901	.9724	1.0651	.....	1.0031	1.0394	1.0775	1.1237
200	"	1.1302	1.1961	1.2871	.9903	.9739	1.0648	.8431	.9978	1.0251	1.0667	1.1216
400	"	1.1300	1.1965	1.2874	.9928	.9756	1.0636	.8413	.9919	1.0155	1.0546	1.1185
760	"	1.1307	1.1980	1.2899	.9932	.9774	1.0633	.8411	.9859	1.0061	1.0492	1.1151
1000	"	1.1310	1.1981	1.2891	.9936	.9781	1.0617	.8405	.9829	1.0012	1.0380	1.1133
1500	"	1.1314	1.1985	1.2891	.9944	.9795	1.0618	.8401	.9772	.9937	1.0293	1.1102
2000	"	1.1316	1.1985	1.2893	.9950	.9808	1.0618	.8397	.9704	.9884	1.0229	1.1082
3000	"	1.1321	1.1988	1.2890	.9963	.9826	1.0607	.8394	.9667	.9801	1.0117	1.1045
4000	"	1.1324	1.1986	1.2875	.9969	.9835	1.0599	.8390	.9618	.9738	1.0051	1.1010
5000	"	1.1325	1.1982	.....	.9975	.9844	1.0597	.8392	.9578	.9686	1.0020	1.0981
6000	"	1.1322	1.1977	.....	.9983	.9854	1.0586	.8393	.9544	.9645	.9977	1.0955
7000	"	1.1318	1.1971	.....	.9986	.9856	1.0592	.8375	.9512	.9607	.9937	1.0927
8000	"	1.1315	1.1965	.....	.9987	.9864	1.0585	.8370	.9485	.9577	.9904	1.0905
10000	"	1.1307	.....	.....	.9994	.9878	1.0573	.8362	.9433	.9522	.9848	1.0862
12000	"	1.1304	.....	.....	1.0001	.9888	1.0579	.8356	.9393	.9477	.9807	1.0827
15000	"	1.1299	.....	.....	1.0007	.9893	1.0578	.8346	.9340	.9419	.9754	1.0777
20000	"	1.1300	.....	.....	1.0015	.9910	1.0574	.8343	.9260	.9347	.9690	1.0718
25000	"	1.1301	.....	.....	1.0021	.9925	1.0573	.8348	.9230	.9294	.9649	1.0678
28000	"	1.1299	.....	.....	1.0028	.9933	1.0576	.8351	.9209	.9265	.9631	1.0661
30000	"	1.1300	.....	.....	1.0029	.9932	1.0574	.8349	.9192	.9248	.9618	1.0642
32000	"	1.1301	.....	.....	1.0032	.9937	1.0572	.8350	.9178	.9235	.9606	1.0634
33012	"	.....	.....	.....	1.0035	.9939	1.0575	.8353	.9168	.9223	.9592	1.0626
Mean Ratios.												
		1.1309	1.1976	1.2885								
		1.002	1.002	1.002	1.014	1.025	1.010	1.011	1.105	1.138	1.146	1.061

Ratio of Highest to Lowest Ratio.

TABLE XI.  
Ratios of Vapour-Pressures to those of Fluorobenzene at corresponding Temperatures.

Temp. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$COCl_2.$	$SnCl_4.$	$(C_2H_5)_2O.$	$OH_2OH.C_6H_5OH.$	$C_6H_5OH.$	$OH.OOOH.$
273-25	1.0000	.998	.987	.985	1.338	1.460	.706	.....	.....	.....	.476
286.3	"	1.008	1.012	1.002	1.309	1.390	.727	.....	.359	.999	.495
308.9	"	1.016	1.012	1.010	1.288	1.346	.741	.....	.417	.982	.562
320.25	"	1.015	1.010	1.013	1.265	1.297	.758	.705	.493	.182	.612
338.75	"	1.014	1.008	1.007	1.239	1.258	.772	.728	.579	.247	.658
358.1	"	1.005	.998	.998	1.200	1.206	.778	.740	.409	.323	.708
367.3	"	1.001	.994	.998	1.183	1.189	.784	.746	.727	.365	.740
382.0	"	.999	.994	.996	1.177	1.160	.794	.753	.807	.434	.784
393.25	"	.998	.991	.994	1.163	1.136	.799	.758	.....	.587	.817
410.4	"	.993	.988	.997	1.144	1.117	.805	.761	.966	.573	.859
423.8	"	.992	.992	1.007	1.136	1.101	.810	.769	1.049	.637	.897
434.85	"	.990	.994	.....	1.127	1.090	.813	.774	1.112	.691	.931
444.25	"	.991	.996	.....	1.120	1.077	.814	.775	1.167	.735	.956
452.8	"	.997	1.002	.....	1.119	1.074	.816	.782	1.217	.778	.985
460.4	"	1.000	1.007	.....	1.114	1.066	.821	.785	1.269	.810	1.006
473.6	"	1.002	.....	.....	1.108	1.056	.823	.791	1.335	.858	1.047
484.95	"	1.004	.....	.....	1.102	1.047	.825	.795	1.399	.913	1.083
499.7	"	1.009	.....	.....	1.095	1.041	.827	.801	1.466	.967	1.130
519.7	"	1.007	.....	.....	1.088	1.029	.828	.804	1.533	1.028	1.190
536.0	"	1.008	.....	.....	1.083	1.019	.829	.802	1.596	1.071	1.229
544.5	"	1.006	.....	.....	1.078	1.012	.828	.800	1.651	1.065	1.246
550.0	"	1.008	.....	.....	1.077	1.013	.829	.800	1.725	1.086	1.264
568.0	"	1.007	.....	.....	1.076	1.009	.829	.801	1.745	1.109	1.272
569.55	"	.....	.....	.....	1.073	1.008	.828	.798	1.762	1.124	1.280
Ratio of Highest to Lowest Ratio.											
{ 1.026   1.025   1.028   1.247   1.448   1.174   1.140   4.91   7.02   11.35   2.68											

TABLE XII.  
Ratios of Molecular Volumes of Liquid to those of Fluorbenzene at corresponding Pressures.

Pressure $C_6H_5F$ .	$O_6H_5F$ .	$O_6H_5Cl$ .	$O_6H_5Br$ .	$O_6H_5I$ .	$C_6H_6$ .	$OCl_4$ .	$SnCl_4$ .	$(C_2H_5)_2O$ .	$CH_3OH$ .	$C_2H_5OH$ .	$CH_3OOH$ .
20	1.0000	1.1248	1.1806	1.2768	.9413	.....	1.2700	.....	.....	.8198	.6324
50	"	1.1241	1.1794	1.2758	.9418	1.0173	1.2718	.....	.4317	.8166	.6324
100	"	1.1234	1.1788	1.2757	.9420	1.0176	1.2724	.....	.4295	.8143	.6327
200	"	1.1234	1.1787	1.2760	.9425	1.0176	1.2740	.....	.4293	.8115	.6336
400	"	1.1239	1.1793	1.2769	.9441	1.0183	1.2773	1.0319	.4294	.8083	.6345
760	"	1.1247	1.1806	1.2785	.9441	1.0190	1.2777	1.0330	.4274	.8053	.6358
1000	"	1.1249	1.1805	1.2785	.9438	1.0191	1.2781	1.0332	.4268	.8037	.6362
1500	"	1.1249	1.1809	1.2788	.9439	1.0199	1.2795	1.0333	.4259	.8012	.6366
2000	"	1.1238	1.1798	1.2778	.9436	1.0197	1.2793	1.0324	.4247	.7987	.6364
3000	"	1.1241	1.1802	1.2781	.9442	1.0200	1.2804	1.0315	.4235	.7966	.6363
4000	"	1.1244	1.1799	1.2780	.9442	1.0197	1.2792	1.0305	.4222	.7953	.6357
5000	"	1.1243	1.1800	.....	.9436	1.0190	1.2794	1.0301	.4211	.7936	.6359
6000	"	1.1252	1.1808	.....	.9441	1.0191	1.2799	1.0311	.4210	.7934	.6354
7000	"	1.1254	1.1814	.....	.9441	1.0183	1.2810	1.0317	.4202	.7927	.6353
8000	"	1.1249	1.1814	.....	.9436	1.0180	1.2810	1.0324	.4198	.7924	.6349
10000	"	1.1254	.....	.....	.9433	1.0188	1.2818	1.0343	.4188	.7918	.6348
12000	"	1.1265	.....	.....	.9437	1.0201	1.2854	1.0354	.4182	.7918	.6350
15000	"	.....	.....	.....	.9457	1.0200	1.2877	1.0341	.4172	.7915	.6335
20000	"	1.1310	.....	.....	.9457	1.0214	1.2910	1.0327	.4173	.7919	.6331
25000	"	1.1310	.....	.....	.9460	1.0248	.....	1.0364	.4173	.7933	.6319
28000	"	1.1310	.....	.....	.9448	1.0248	.....	1.0403	.4188	.7937	.6342
30000	"	1.1270	.....	.....	.9448	1.0222	.....	1.0397	.4183	.7944	.6321
32000	"	1.1350	.....	.....	.9446	1.0169	.....	1.0456	.4222	.7978	.6311
33912	"	.....	.....	.....	.9400	.....	.....	.....	.....	.....	.6310
Mean Ratios.											
Ratio of Highest to Lowest Ratio.											
1	*1.1246	1.1802	1.2772	.9439	1.0195	1.2793	1.0342	.4228	.6153	.7995	.6342
1	*1.003	1.002	1.002	1.002	1.006	1.008	1.017	1.015	1.035	1.041	1.009

\* Omitting approximate values.

TABLE XIII.

Ratios of Molecular Volumes of Liquid to those of Fluorobenzene at corresponding Temperatures.

Temp. $C_6H_5F$	$O_6H_5F$	$C_6H_5Cl$	$C_6H_5Br$	$C_6H_5I$	$C_6H_6$	$COCl_2$	$SnCl_4$	$(C_6H_5)_2O$	$CH_3OH$	$C_2H_5OH$	$C_3H_7OH$	$CH_3COOH$
272.25	1.0000	1.1247	1.1802	1.2761	.9457	.....	1.2657	.....	.....	.....	.....	.6215
289.3	"	1.1242	1.1794	1.2758	.9462	1.0250	1.2673	.....	.....	.....	.7865	.6203
303.9	"	1.1240	1.1792	1.2760	.9467	1.0254	1.2689	.....	.....	.6044	.7837	.6198
320.25	"	1.1239	1.1790	1.2765	.9476	1.0260	1.2705	.....	.4160	.6022	.7809	.6197
338.75	"	1.1244	1.1798	1.2772	.9485	1.0267	1.2720	1.0284	.4152	.5997	.7783	.6197
358.1	"	1.1238	1.1805	1.2782	.9487	1.0273	1.2744	1.0297	.4136	.5971	.7748	.6198
367.3	"	1.1250	1.1802	1.2783	.9487	1.0278	1.2743	1.0299	.4127	.5958	.7732	.6201
382.0	"	1.1248	1.1804	1.2784	.9489	1.0283	1.2763	1.0301	.4115	.5939	.7709	.6203
393.25	"	1.1236	1.1792	1.2773	.9484	1.0280	1.2761	1.0290	.4102	.5919	.7684	.6196
410.4	"	1.1236	1.1793	1.2777	.9489	1.0280	1.2775	1.0279	.4087	.5895	.7661	.6191
423.8	"	1.1236	1.1789	1.2789	.9491	1.0275	1.2769	1.0273	.4078	.5880	.7664	.6185
434.85	"	1.1234	1.1793	.....	.9484	1.0266	1.2773	1.0272	.4068	.5871	.7636	.6179
444.25	"	1.1242	1.1804	.....	.9487	1.0264	1.2786	1.0279	.4061	.5867	.7639	.6178
452.8	"	1.1252	1.1815	.....	.9489	1.0264	1.2791	1.0291	.4054	.5864	.7638	.6174
460.4	"	1.1252	1.1815	.....	.9489	1.0264	1.2791	1.0291	.4054	.5864	.7638	.6174
473.6	"	1.1260	.....	.....	.9478	1.0262	1.2822	1.0331	.4041	.5855	.7646	.6171
484.95	"	1.1280	.....	.....	.9477	1.0270	1.2844	1.0345	.4040	.5851	.7660	.6178
499.7	"	.....	.....	.....	.9483	1.0271	1.2867	1.0326	.4038	.5859	.7677	.6188
519.7	"	.....	.....	.....	.9489	1.0281	1.2913	1.0357	.4047	.5845	.7711	.6204
536.0	"	1.1360	.....	.....	.9508	1.0279	.....	1.0377	.4060	.5894	.7737	.6203
544.5	"	1.1360	.....	.....	.9489	1.0280	.....	1.0421	.4082	.5900	.7760	.6227
550.0	"	1.1370	.....	.....	.9476	1.0260	.....	1.0430	.4104	.5941	.7776	.6251
555.0	"	1.1520	.....	.....	.9482	1.0188	.....	1.0483	.4167	.6017	.7817	.6259
559.55	"	.....	.....	.....	.9400	.....	.....	.....	.....	.....	.....	.6310
Mean Ratios.												
	*1.1245	1.1800	1.2773	.9479	1.0286	1.277	1.033	.409	.592	.772	.623	
Ratio of Highest to Lowest Ratio.												
	*1.004	1.003	1.002	1.011	1.009	1.020	1.021	1.032	1.030	1.034	1.023	

\* Omitting approximate values.

TABLE XIV.

Ratios of Molecular Volumes of Saturated Vapour to those of Fluorobenzene at corresponding Pressures.

Pressure $C_6H_5F$ .	$C_6H_5F$ .	$C_6H_5Cl$ .	$C_6H_5Br$ .	$C_6H_5I$ .	$C_6H_6$ .	$CCl_4$ .	$SnCl_4$ .	$(C_2H_5)_2O$ .	$CH_3OH$ .	$C_2H_5OH$ .	$C_2H_5OH$ .	$OH, COOH$ .
1000	1.000	1.120	1.168	1.269	.925	.960	1.278	1.036	.583	.706	.903	.545
1500	"	1.128	1.175	1.279	.930	.970	1.276	1.037	.530	.700	.895	.562
2000	"	1.133	1.179	1.283	.933	.973	1.277	1.036	.527	.701	.898	.557
3000	"	1.141	1.189	1.289	.942	.983	1.281	1.038	.525	.697	.880	.565
4000	"	1.143	1.195	1.290	.951	.992	1.287	1.038	.522	.696	.874	.571
5000	"	1.145	1.196	.....	.954	.997	1.282	1.038	.520	.694	.872	.577
6000	"	1.143	1.199	.....	.958	1.002	1.286	1.038	.517	.693	.870	.582
7000	"	1.144	1.199	.....	.961	.999	1.283	1.037	.515	.690	.868	.584
8000	"	1.143	1.200	.....	.961	.995	1.288	1.037	.513	.688	.866	.588
10000	"	1.138	.....	.....	.960	.997	1.302	1.041	.511	.688	.866	.596
12000	"	1.131	.....	.....	.955	.994	1.282	1.040	.507	.675	.867	.599
15000	"	.....	.....	.....	.947	.995	1.272	1.042	.503	.665	.849	.607
20000	"	.....	.....	.....	.944	1.002	1.262	1.042	.495	.645	.829	.623
25000	"	.....	.....	.....	.940	1.000	.....	1.035	.480	.638	.810	.623
28000	"	.....	.....	.....	.936	.983	.....	1.035	.472	.643	.814	.622
30000	"	.....	.....	.....	.946	1.006	.....	1.050	.475	.643	.825	.630
32000	"	.....	.....	.....	.....	1.017	.....	1.032	.478	.625	.896	.625
33012	"	.....	.....	.....	.940	.....	.....	.....	.....	.....	.....	.631
Mean Ratios.												
		1.137	1.189	1.282	.946	.993	1.282	1.038	.507	.676	.859	.593
Ratio of Highest to Lowest Ratio.												
		1.022	1.027	1.017	1.039	1.059	1.032	1.010	1.129	1.130	1.115	1.153

TABLE XV.

Ratio of Molecular Volumes of Saturated Vapour to those of Fluorbenzene at corresponding Temperatures.

Temp. $O_6H_3F.$	$C_6H_3F.$	$C_6H_3Cl.$	$C_6H_3Br.$	$C_6H_3I.$	$O_6H_3.$	$COCl_4.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.$	$C_2H_5OH.$	$O_3H_3OH.$	$OH_3COOH.$
367.3	1.000	1.118	1.174	1.272	.842	.828	1.336	1.101	1.244	2.076	2.678	.894
382.0	"	1.130	1.186	1.286	.853	.852	1.329	1.092	1.126	1.905	2.254	.884
393.25	"	1.135	1.189	1.292	.866	.866	1.322	1.088	1.049	1.835	2.007	.845
410.4	"	1.150	1.201	1.293	.885	.895	1.316	1.083	.945	1.414	1.714	.818
423.8	"	1.150	1.203	1.281	.893	.910	1.313	1.078	.875	1.284	1.541	.797
434.85	"	1.156	1.203	.....	.906	.924	1.308	1.073	.826	1.191	1.422	.782
444.25	"	1.155	1.204	.....	.919	.933	1.305	1.067	.788	1.126	1.337	.769
452.8	"	1.146	1.199	.....	.917	.935	1.300	1.059	.755	1.071	1.266	.756
460.4	"	1.143	1.189	.....	.923	.938	1.300	1.048	.729	1.028	1.216	.745
473.6	"	1.134	.....	.....	.927	.949	1.300	1.048	.689	.962	1.139	.729
484.95	"	1.116	.....	.....	.931	.954	1.291	1.041	.655	.908	1.081	.712
499.7	"	.....	.....	.....	.926	.959	1.275	1.040	.615	.841	1.016	.694
519.7	"	.....	.....	.....	.926	.977	1.262	1.030	.572	.763	.943	.681
536.0	"	.....	.....	.....	.924	.982	.....	1.028	.530	.705	.875	.665
544.5	"	.....	.....	.....	.930	.985	.....	1.030	.508	.690	.861	.653
550.0	"	.....	.....	.....	.940	.995	.....	1.041	.497	.676	.864	.649
555.0	"	.....	.....	.....	.....	1.014	.....	1.025	.484	.648	.866	.639
559.55	"	.....	.....	.....	.940	.....	.....	.....	.....	.....	.....	.631
Mean Ratios.												
				1.285	Ratio of Highest to Lowest Ratio.							
				1.194	1.116	1.224	1.059	1.074	2.570	3.204	3.110	1.417
				1.036	1.026	1.017	1.026	1.074	2.570	3.204	3.110	1.417



TABLE XVI.

Percentage-differences between Highest and Lowest Ratios in each comparison with Fluorobenzene.

	$C_6H_5Cl$	$C_6H_5Br$	$C_6H_5I$	$C_6H_6$	$COCl_2$	$SnCl_4$	$(C_2H_5)_2O$	$CH_3OH$	$C_2H_5OH$	$C_6H_5OH$	$C_6H_5OCH_3$	$CH_3COOH$
Absolute temperatures at corresponding pressures	0.2	0.2	0.2	1.4	2.5	1.0	1.1	10.5	13.8	14.6		6.1
Vapour-pressures at corresponding temperatures...	2.6	2.5	2.8	24.7	44.8	17.4	14.0	391.0	602.0	1035.0		188.5
Molecular volumes of liquid at corresponding pressures .....	0.3	0.2	0.2	0.6	0.8	1.7	1.5	3.5	4.1	3.6		0.9
Molecular volumes of liquid at corresponding temperatures .....	0.4	0.3	0.2	1.1	0.9	2.0	2.1	3.2	3.0	3.4		2.3
Molecular volumes of saturated vapour at corresponding pressures .....	2.2	2.7	1.7	3.9	5.9	3.2	1.0	12.9	13.0	11.5		15.8
Molecular volumes of saturated vapour at corresponding temperatures...	3.6	2.6	1.7	11.6	22.4	5.9	7.4	157.0	220.4	211.0		41.7

N 2

The degree of deviation from constancy of the various ratios is indicated by the values given at the foot of each table, representing the ratio of the highest to the lowest ratio in each vertical column. These values are collected together in Table XVI. (p. 171), but for the sake of greater clearness they are given as percentage-differences between the highest and lowest ratios in each case, the lowest ratio being always taken as 100.

It will be seen that the halogen derivatives of benzene show very much smaller deviations from constancy than the other compounds; and I have previously suggested (*Trans. Chem. Soc.* 1889, p. 486; 1891, p. 125) that the generalizations of Van der Waals do hold good for these bodies, in which case the deviations of the ratios from constancy may be taken as an approximate measure of the experimental errors to be expected with other compounds. It must, however, be admitted that the mean ratios of the absolute temperatures differ sensibly from the mean ratios of the molecular volumes of liquid, though they should be identical if Van der Waals's generalizations were strictly true, while the errors in these determinations are probably very small. Indeed, in the comparison of bromobenzene with fluorobenzene the difference between the mean ratios amounts to 1.5 per cent. (Table XXI.), while the difference between the highest and lowest ratio in either case is only 0.2 per cent. (Table XVI.). It is probable, therefore, that the generalizations of Van der Waals are not quite, though very nearly, true for these bodies.

The deviations from constancy are smallest in the comparisons of the absolute temperatures at corresponding pressures, and of the molecular volumes of liquid at corresponding pressures and temperatures; and this is no doubt to be expected, since the ratio of the highest to the lowest absolute temperature or volume of liquid for any one substance does not amount to 3 : 1, whereas the ratio of the highest to the lowest pressure is from 1700 to 10000 : 1, and of the highest to the lowest molecular volume of saturated vapour from 3.7 : 1 in the case of iodobenzene, where the range is limited, to 2670 to 1 with acetic acid. It is also impossible to determine the volumes of saturated vapour with anything like the same degree of accuracy as the volumes of liquid, the liability to error by the new method being especially great at the lowest temperatures.

The eleven substances which are compared with fluorobenzene may be arranged in three groups as below:—

1. *Chlorobenzene, Bromobenzene, Iodobenzene.*—As already pointed out, the generalizations of Van der Waals are very nearly true for these bodies when compared with fluorobenzene.

2. *Benzene, Carbon tetrachloride, Stannic chloride, Ether.*—With these substances the generalizations may be taken as

rough approximations to the truth, but the deviations of the ratios from constancy are in most cases much too large to be attributed to error of experiment.

3. *The three Alcohols and Acetic Acid.*—The majority of the generalizations do not hold good at all; the deviations of the ratios from constancy are, however, not very great in the case of the molecular volumes of liquid at corresponding pressures and temperatures.

#### *Discussion of the Generalizations.*

1. *Corresponding Temperatures and Pressures.*—It must, I think, be concluded that the statement that "if the absolute temperatures of various substances are proportional to their absolute critical temperatures their vapour-pressures will be proportional to their critical pressures" has not been proved by experiment to be true except in a very limited number of cases; indeed, when the alcohols and acetic acid are compared with fluorbenzene, the statement is quite wide of the mark. It follows, therefore, that in the comparison of the molecular volumes the ratios at corresponding pressures must differ from those at corresponding temperatures.

2. *Molecular Volumes of Liquid.*—The deviations of the ratios from constancy are smaller in this case than in any of the others, but are certainly not within the limits of experimental error. The comparisons at corresponding pressures seem to be somewhat better on the whole than at corresponding temperatures, but the difference is not very marked.

3. *Molecular Volumes of Saturated Vapour.*—At corresponding pressures the deviations from constancy are within the limits of experimental error in the case of ether and stannic chloride, and are relatively small for benzene and carbon tetrachloride.

There can be no doubt that with the saturated vapours the comparisons at corresponding pressures are very much better than at corresponding temperatures; and it may therefore be concluded that it is better to compare the molecular volumes both of liquid and of saturated vapour at corresponding pressures than at corresponding temperatures.

#### *Saturated Vapours.*

It has been pointed out (Trans. Chem. Soc. 1891, p. 137) that if the generalizations of Van der Waals were strictly true, it would follow that the ratios of the actual densities of the saturated vapours of different substances to their theoretical densities should be equal at corresponding pressures; and as this method of comparison is a very convenient one I have thought it worth while to tabulate the ratios, although it has already been shown that the relation cannot be strictly true. The values for benzene and its halogen derivatives have

TABLE XVII.

Ratios of Actual to Theoretical Densities of Saturated Vapour at corresponding Pressures.

Pressure. $C_6H_5F.$	$C_6H_5F.$	$C_6H_5Cl.$	$C_6H_5Br.$	$C_6H_5I.$	$C_6H_6.$	$OOl_4.$	$SnCl_4.$	$(C_2H_5)_2O.$	$CH_3OH.C_2H_5OH.$	$C_2H_5OH.$	$CH_3COOH.$
20	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.907
50	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.829
100	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.770
200	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.718
400	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.678
760	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.657
1000	1.037	1.047	1.063	1.053	1.037	1.047	1.040	1.029	1.050	1.025	1.047
1500	1.046	1.059	1.077	1.065	1.052	1.059	1.063	1.054	1.071	1.040	1.064
2000	1.073	1.072	1.091	1.079	1.068	1.073	1.079	1.072	1.105	1.081	1.089
3000	1.107	1.099	1.116	1.107	1.091	1.098	1.107	1.090	1.122	1.099	1.099
4000	1.138	1.127	1.142	1.136	1.112	1.122	1.136	1.153	1.157	1.132	1.090
5000	1.166	1.153	1.168	.....	1.136	1.147	1.162	1.180	1.189	1.164	1.173
6000	1.193	1.181	1.192	.....	1.159	1.173	1.187	1.207	1.219	1.192	1.192
7000	1.217	1.206	1.217	.....	1.180	1.197	1.213	1.233	1.277	1.242	1.781
8000	1.247	1.233	1.242	.....	1.206	1.233	1.238	1.260	1.306	1.287	1.805
10000	1.300	1.291	.....	.....	1.260	1.275	1.287	1.308	1.360	1.315	1.852
12000	1.349	1.347	.....	.....	1.316	1.329	1.343	1.358	1.419	1.373	1.904
15000	1.431	.....	.....	.....	1.408	1.410	1.435	1.436	1.507	1.462	1.983
20000	1.600	.....	.....	.....	1.582	1.571	1.619	1.605	1.700	1.664	2.153
25000	1.818	.....	.....	.....	1.806	1.790	.....	1.837	1.985	1.927	2.434
28000	2.011	.....	.....	.....	2.006	1.994	.....	2.032	2.228	2.116	2.691
30000	2.206	.....	.....	.....	2.180	2.164	.....	2.199	2.420	2.282	2.920
32000	2.450	.....	.....	.....	.....	2.376	.....	2.485	2.699	2.504	3.252
33912	4.400	.....	.....	.....	4.370	.....	.....	.....	.....	.....	5.792
		(4.43)	(4.46)	(4.43)	4.370	(4.30)	(4.35)	(4.40)	(5.18)	(4.70)	

The bracketed values are calculated from the molecular critical volumes given in Table XXII.

already been published (*loc. cit.*); but there are one or two obvious small irregularities, and I have therefore mapped the ratios against temperature and constructed curves for each substance (Plate I.). The smoothed values read from the curves are given in this paper, and the molecular volumes of saturated vapour have also been recalculated from the density ratios. The same method of procedure has been adopted with the other substances.

The close similarity in the behaviour of the halogen derivatives of benzene and the approximate agreement in the case of the members of Group II. is very clearly shown in Table XVII.

It is generally admitted that gaseous acetic acid at low temperatures contains molecules more complex than those corresponding to the ordinary formula  $C_2H_4O_2$ , and from the very high density at the critical point it would appear that many of these complex molecules have escaped dissociation even at this high temperature.

It will be seen that with the alcohols the differences from the other substances become generally more marked as the critical point is approached. At the highest pressure the vapour-density of methyl alcohol is very distinctly higher than that of any member of the first or second group at the corresponding pressure; and this fact appears to favour the conclusion of M. Guye and others, that some of the molecules of methyl alcohol at the critical point and in the liquid state at all temperatures are more complex than in the ordinary gaseous state. On the other hand, by a comparison of the densities of the saturated vapours of acetic acid with those of the alcohols and ether, Dr. Ramsay and I were led to the conclusion that the molecules of ordinary substances, including the alcohols, are not more complex in the liquid than in the gaseous state. This conclusion, so far as the members of Groups I. and II. are concerned, is strengthened by the results given in the preceding Table; but it is certainly weakened to some extent in the case of the alcohols, or at any rate of methyl alcohol.

There is no doubt that these bodies do show marked differences in many of their properties from the majority of compounds; and the most plausible explanation of these differences seems to be the existence of complex molecules in the liquid state, although there is ample proof that they are not present in the saturated vapours at low temperatures.

As the alcohols differ so widely from other substances, it is of interest to find whether the relations of Van der Waals hold good when they are compared among themselves. I have therefore calculated the ratios of the absolute temperatures, pressures, and volumes of ethyl and propyl alcohol to methyl alcohol and of propyl alcohol to ethyl alcohol. The results are given in the following Tables:—

TABLE XVIII.—Alcohols at corresponding Pressures.

Pressures of $C_2H_5OH$ .	Absolute Temperatures.			Molecular Volumes of Liquid.			Molecular Volumes of Vapour.		
	$\frac{C_2H_5OH}{CH_3OH}$ .	$\frac{C_2H_5OH}{CH_3OH}$ .	$\frac{C_2H_5OH}{C_2H_5OH}$ .	$\frac{C_2H_5OH}{CH_3OH}$ .	$\frac{C_2H_5OH}{CH_3OH}$ .	$\frac{C_2H_5OH}{C_2H_5OH}$ .	$\frac{C_2H_5OH}{CH_3OH}$ .	$\frac{C_2H_5OH}{C_2H_5OH}$ .	$\frac{C_2H_5OH}{C_2H_5OH}$ .
20	1.0863	1.0860	1.0479	.....	1.2998	.....	.....	.....	.....
50	1.0827	1.0785	1.0443	1.4565	1.2989	.....	.....	.....	.....
100	1.0302	1.0741	1.0427	1.4597	1.2989	.....	.....	.....	.....
200	1.0274	1.0690	1.0405	1.4562	1.2981	.....	.....	.....	.....
400	1.0238	1.0632	1.0385	1.4546	1.2971	.....	.....	.....	.....
760	1.0205	1.0581	1.0368	1.4535	1.2962	.....	.....	.....	.....
1000	1.0187	1.0561	1.0367	1.4527	1.2962	.....	.....	.....	.....
1500	1.0169	1.0533	1.0358	1.4515	1.2960	.....	.....	.....	.....
2000	1.0186	1.0541	1.0349	1.4480	1.2963	.....	.....	.....	.....
3000	1.0139	1.0465	1.0322	1.4493	1.2977	.....	.....	.....	.....
4000	1.0125	1.0450	1.0321	1.4494	1.2959	.....	.....	.....	.....
5000	1.0113	1.0461	1.0344	1.4555	1.2946	.....	.....	.....	.....
6000	1.0106	1.0454	1.0344	1.4543	1.2958	.....	.....	.....	.....
7000	1.0100	1.0447	1.0344	1.4558	1.2957	.....	.....	.....	.....
8000	1.0097	1.0442	1.0341	1.4538	1.2963	.....	.....	.....	.....
10000	1.0094	1.0440	1.0348	1.4543	1.3001	.....	.....	.....	.....
12000	1.0090	1.0441	1.0348	1.4541	1.3021	.....	.....	.....	.....
15000	1.0084	1.0443	1.0356	1.4534	1.3054	.....	.....	.....	.....
20000	1.0093	1.0465	1.0368	1.4572	1.3023	.....	.....	.....	.....
25000	1.0070	1.0455	1.0382	1.4576	1.3044	.....	.....	.....	.....
28000	1.0061	1.0458	1.0394	1.4466	1.3102	.....	.....	.....	.....
30000	1.0061	1.0464	1.0400	1.4540	1.3043	.....	.....	.....	.....
32000	1.0063	1.0467	1.0402	1.4482	1.3049	.....	.....	.....	.....
33912	1.0060	1.0462	1.0399	.....	.....	.....	.....	.....	.....
Mean Ratios.									
	1.030	1.040	1.015	1.4534	1.8690	1.2999	1.329	1.693	1.274
	Ratio of Highest to Lowest Ratio.								
	1.030	1.040	1.015	1.012	1.013	1.012	1.040	1.057	1.068

TABLE XIX.—Alcohols at corresponding Temperatures.

Absolute Temperatures of $C_6H_5F$ .	Vapour-Pressures.			Molecular Volumes of Liquid.			Molecular Volumes of Saturated Vapour.		
	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_3H_7OH}{CH_3OH}$	$\frac{C_4H_9OH}{C_2H_5OH}$	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_3H_7OH}{CH_3OH}$	$\frac{C_4H_9OH}{C_2H_5OH}$	$\frac{C_2H_5OH}{CH_3OH}$	$\frac{C_3H_7OH}{CH_3OH}$	$\frac{C_4H_9OH}{C_2H_5OH}$
272-25	.....	.....	....	.....	.....	.....	.....	.....	.....
289-3	.....	.....	.....	.....	.....	.....	.....	.....	.....
308-9	.....	.....	.....	.....	.....	.....	.....	.....	.....
320-25	.....	.....	.....	.....	.....	.....	.....	.....	.....
338-75	.....	.....	.....	.....	.....	.....	.....	.....	.....
358-1	.....	.....	.....	.....	.....	.....	.....	.....	.....
367-3	.....	.....	.....	.....	.....	.....	.....	.....	.....
382-0	.....	.....	.....	.....	.....	.....	.....	.....	.....
393-25	.....	.....	.....	.....	.....	.....	.....	.....	.....
410-4	.....	.....	.....	.....	.....	.....	.....	.....	.....
423-8	.....	.....	.....	.....	.....	.....	.....	.....	.....
434-85	.....	.....	.....	.....	.....	.....	.....	.....	.....
444-25	.....	.....	.....	.....	.....	.....	.....	.....	.....
452-8	.....	.....	.....	.....	.....	.....	.....	.....	.....
460-4	.....	.....	.....	.....	.....	.....	.....	.....	.....
473-6	.....	.....	.....	.....	.....	.....	.....	.....	.....
484-95	.....	.....	.....	.....	.....	.....	.....	.....	.....
499-7	.....	.....	.....	.....	.....	.....	.....	.....	.....
519-7	.....	.....	.....	.....	.....	.....	.....	.....	.....
536-0	.....	.....	.....	.....	.....	.....	.....	.....	.....
544-5	.....	.....	.....	.....	.....	.....	.....	.....	.....
550-0	.....	.....	.....	.....	.....	.....	.....	.....	.....
555-0	.....	.....	.....	.....	.....	.....	.....	.....	.....
559-55	.....	.....	.....	.....	.....	.....	.....	.....	.....
Ratio of Highest to Lowest Ratio.									
	1-658	2-362	1-276	1-009	1-018	1-015	1-895	1-306	1-129

The percentage difference between the highest and lowest ratios in the various comparisons—including those with fluorbenzene—are given in the following Table:—

TABLE XX.

	$\frac{\text{CH}_3\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{C}_6\text{H}_5\text{F}}$	$\frac{\text{C}_2\text{H}_5\text{OH}}{\text{CH}_3\text{OH}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{CH}_3\text{OH}}$	$\frac{\text{C}_3\text{H}_7\text{OH}}{\text{C}_2\text{H}_5\text{OH}}$
Absolute temperatures at corresponding pressures.....	10.5	13.8	14.6	3.0	4.0	1.5
Vapour-pressures at corresponding temperatures.....	391.0	602.0	1035.0	65.8	136.2	27.6
Molecular volumes of liquid at corresponding pressures	3.5	4.1	3.6	1.2	1.3	1.2
Molecular volumes of liquid at corresponding temperatures	3.2	3.0	3.4	0.9	1.8	1.5
Molecular volumes of saturated vapour at corresponding pressures .....	12.9	13.0	11.5	4.0	5.7	6.3
Molecular volumes of saturated vapour at corresponding temperatures .....	157.0	220.4	211.0	39.5	30.6	12.9

When the alcohols are compared with one another, the deviations of the ratios from constancy are much smaller than when fluorbenzene is taken as the standard substance, but they are still far outside the limits of experimental error. It may, perhaps, be said—as with the members of Group II. in the comparisons with fluorbenzene—that the generalizations offer a rough approximation to the truth.

Here, again, the comparison of the molecular volumes of saturated vapour at corresponding pressures is very much more satisfactory than at corresponding temperatures.

In the *Philosophical Magazine* for November 1890, p 417, it was pointed out by Prof. Orme Masson that the ratio of the molecular volumes (in the liquid state) of any two members of certain groups of nearly related carbon compounds, at their boiling-points under equal pressure, is equal to the ratio of those boiling-points, expressed on the absolute scale of temperature, or

$$\frac{V}{V'} = \frac{T}{T'}.$$

In the same number of the *Philosophical Magazine* (p. 423) I showed that Masson's relation is a special case of a more general one which should hold good if the generalizations of



Van der Waals were strictly true. This relation may be expressed by the equations

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p},$$

where  $v$  and  $v'$  are the molecular volumes of saturated vapour,  $V$  and  $V'$  those of liquid, and  $T$  and  $T'$  the boiling-points on the absolute scale of any two substances at corresponding pressures  $p$  and  $p'$ .

When the critical pressures are equal  $p=p'$  and the equations become

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'},$$

or the molecular volumes, whether of liquid or saturated vapour, at the boiling-points under equal pressure are proportional to the boiling-points expressed on the absolute scale.

That the relation cannot be strictly true when the critical pressures are different is obvious, since it is not generally true that the vapour-pressures at corresponding temperatures are corresponding pressures. It is still possible, however, that the relation may be true for the critical temperatures, pressures, and volumes. Unfortunately, the critical volumes have only been determined in a few cases, but it has been shown that the ratios of the molecular volumes at corresponding pressures do not vary within very wide limits; and it is, therefore, possible to test the relation in a limited form, taking the critical temperatures and pressures and the mean ratios of the molecular volumes at corresponding pressures.

A preliminary comparison was given in the paper referred to, but it was very incomplete, and there was a small error in some of the calculations owing to the misplacement of a figure in the critical pressure of fluorbenzene, which was given as 33190 instead of 33910.

As the experimental results have been considerably extended since that time and now include the molecular volumes of the saturated vapours, it is possible to give the Table in a complete form.

TABLE XXI.

Comparison of Values of  $\frac{T}{T'} \times \frac{p'}{p}$  with Mean Ratios of  
Molecular Volumes at corresponding Pressures.

Substances compared.	$\frac{T}{T'} \times \frac{p'}{p}$	Mean Ratios of Molecular Volumes.		Percentage difference between highest and lowest of the three values.
		Liquid.	Saturated Vapour.	
$C_6H_5Cl/C_6H_5F$ .....	1.1308	1.1246	1.137	1.1
$C_6H_5Br/C_6H_5F$ .....	1.1974	1.1802	1.189	1.5
$C_6H_5I/C_6H_5F$ .....	1.2884	1.2772	1.282	0.9
$C_6H_5Br/C_6H_5Cl$ .....	1.0589	1.0495	1.047	1.1
$C_6H_5I/C_6H_5Cl$ .....	1.1394	1.1358	1.132	0.7
$C_6H_5I/C_6H_5Br$ .....	1.0760	1.0822	1.080	0.6
$C_6H_6/C_6H_5F$ .....	.9351	.9439	.946	1.2
$CCl_4/C_6H_5F$ .....	.9861	1.0195	.993	3.4
$SnCl_4/C_6H_5F$ .....	1.2771	1.2793	1.282	0.4
$(C_2H_5)_2O/C_6H_5F$ .....	1.0468	1.0342	1.038	1.2
$CH_3OH/C_6H_5F$ .....	.5203	.4228	.507	23.1
$C_2H_5OH/C_6H_5F$ .....	.6537	.6153	.676	9.9
$C_2H_5OH/C_2H_5F$ .....	.8533	.7995	.859	7.4
$CH_3COOH/C_6H_5F$ ...	.8303	.6342	.593	40.0
$C_2H_5OH/CH_3OH$ .....	1.2564	1.4534	1.329	15.7
$C_2H_5OH/CH_3OH$ .....	1.6401	1.8890	1.693	15.2
$C_2H_5OH/C_2H_5OH$ .....	1.3054	1.2999	1.274	2.5

For the halogen derivatives of benzene  $p=p'$ .

It will be seen that the differences between the three values are not very great, except in the comparisons of the three alcohols and acetic acid with fluorobenzene, and of ethyl and propyl alcohol with methyl alcohol. In the other cases, including the comparison of propyl with ethyl alcohol, the relation

$$\frac{v}{v'} = \frac{V}{V'} = \frac{T}{T'} \times \frac{p'}{p}$$

may be considered as approximately true with the limitations already stated.

The two substances—methyl alcohol and acetic acid, and to a small extent ethyl and propyl alcohol—are clearly exceptional in their behaviour, and it is of interest to note, in comparing these substances with fluorobenzene, that while with acetic acid the ratios of the molecular volumes both of liquid and saturated vapour are very low, with methyl alcohol it is only in the liquid state that this is to be observed. This

may again point to the existence of complex molecules of acetic acid in both the liquid and gaseous states, but of methyl alcohol in the liquid state only, except possibly very near the critical point.

With ethyl and propyl alcohols the ratios of the molecular volumes of liquid to those of fluorbenzene are also low, though not nearly to the same extent as with methyl alcohol.

*Note on the Determination of Critical Constants.*

Of the three critical constants, temperature, pressure, and volume, the first is the most easily determined, for by employing as heating-agents the vapours of pure liquids boiling under known pressures, the temperature is perfectly under control and is easily measured. Moreover, the presence of a very small amount of impurity does not influence the critical temperature of a substance to nearly the same extent as the critical pressure.

The critical pressure may also as a rule be determined without very much difficulty, provided that absence of impurity is ensured, but this point is of the utmost importance. In the case of substances that attack mercury at high temperatures, such as carbon tetrachloride and stannic chloride, the ordinary method of operation requires modification, and the calculations become more laborious, but otherwise the difficulty is not greatly increased.

The determination of the critical volume of a substance, even when perfectly pure and without action on mercury,

Fig. 1.

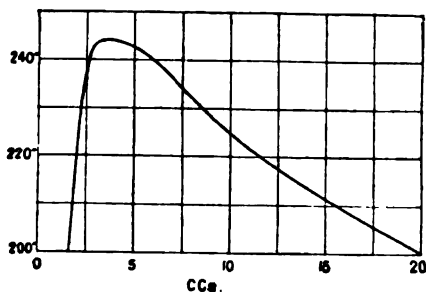
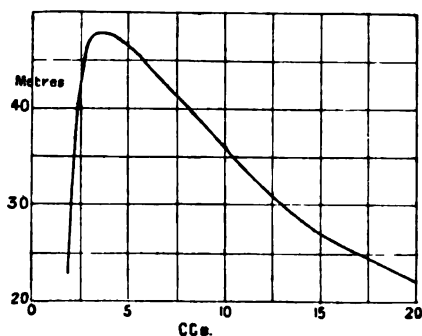


Fig. 2.



is, however, a much more difficult matter. That this is so is evident from the form of the curves representing the relation

of the volumes of liquid and of saturated vapour to the temperature or pressure, as shown in the accompanying diagrams constructed from the results with ethyl alcohol.

A very small alteration of temperature, such as  $0.1^{\circ}$ , at or just below the critical point, produces a considerable alteration in the volume ; therefore in order to obtain a direct reading of the critical volume it is necessary that the substance shall be exactly at its critical temperature.

I have assumed that a substance is in this state when on rapidly increasing the volume somewhat above the critical volume the fall of temperature due to the expansion causes a momentary separation of liquid and vapour.

In order to determine the critical volume, I note the position of this temporary mark of division and then diminish the volume slightly. After waiting a few minutes for the temperature to become constant again, I increase the volume very slightly but rapidly, and again note the position of the mark of division, which is now nearer to the top of the tube. Proceeding in this way it is possible under favourable conditions to make the substance occupy such a volume that a very slight but rapid expansion gives a temporary mark of division of liquid and vapour almost exactly at the top of the tube. This volume I take to be the critical volume, and I have succeeded in determining it directly in the case of benzene, fluorbenzene, and acetic acid ; while with chlorobenzene, for which mercury vapour was employed as a jacket, it was only possible to obtain a rough approximation to the true volume on account of the slight unsteadiness of the temperature.

The critical volumes of the other substances may probably be ascertained with fair accuracy in the following manner :—

At low temperatures and pressures the ratios of the molecular volumes of liquid and saturated vapour of any one substance to those of fluorbenzene at corresponding temperatures and pressures differ somewhat widely as a rule, but as the critical point is approached the differences diminish and at the critical point itself all four values should, of course, be identical. It follows, therefore, that by mapping the ratios against temperature, four straight lines or curves should be obtained, which, when produced, should cut one another at the critical temperature, and the point of intersection should give the ratio of the molecular critical volume to that of fluorbenzene.

It will be seen from the accompanying diagrams, figs. 3 to 6, Plates II. & III., that in the case of benzene and acetic acid the four curves do very nearly cut one another at the critical temperature, and the ratios of the critical volumes thus

obtained agree very well with those calculated from the experimental results. The other substances will be considered in their order.

*Halogen Derivatives of Benzene.*—Accurate determinations of the volumes of liquid have been obtained only up to  $280^{\circ}$ , but the ratios are very nearly constant and are practically identical at corresponding temperatures and pressures; the extrapolation may therefore be considered justifiable. In the case of chlorobenzene a few approximate determinations have been made near the critical temperature; they give slightly higher ratios than those at lower temperatures, and agree rather more closely with the mean ratio of the absolute temperatures at corresponding (equal) pressures.

The molecular volumes of the saturated vapours give generally higher ratios than those of the liquid; this may be partly due to experimental error; but as the deviations are nearly all in the same direction, it seems hardly justifiable to attribute them entirely to this cause. It is evidently impossible to make use of these ratios in determining the critical volumes; but the mean ratios of the molecular volumes of liquid may probably be relied on to give fairly accurate results (Trans. Chem. Soc. lv. p. 517).

*Carbon Tetrachloride.*—As the observations extend to within a few degrees of the critical temperature, there does not seem to be much room for error.

*Stannic Chloride.*—The molecular volumes of saturated vapour cannot be made use of, as the results at the highest temperatures are a little doubtful owing to slight decomposition of the substance; considerable extrapolation would also be necessary. The ratios for the liquid state give, however, very nearly straight lines, which may therefore probably be extrapolated without much error.

*Ether.*—The four curves would evidently be very close together at the critical temperature, but as the results with the saturated vapour are somewhat irregular it seems best to rely only upon those with the liquid.

*Methyl Alcohol.*—In this case the curves for the liquid state do not seem to agree well with those for the saturated vapour; I have taken the mean value, but it is evidently open to some doubt.

*Ethyl and Propyl Alcohols.*—The agreement is better with these alcohols, but the volumes of saturated vapour are somewhat irregular near the critical point.

*Acetic Acid.*—The four curves meet very satisfactorily at the critical temperature.

The mean ratios of the molecular volumes to those of fluor-

benzene are given in the following Table, together with the molecular and specific critical volumes calculated from them, taking the observed critical volume of fluorbenzene as correct. For the sake of comparison the specific volumes directly observed and also those previously adopted by Ramsay and myself are given.

TABLE XXII.

Substance.	Mean Ratio.	Molecular Volume. Calculated.	Specific Volume.		
			Calculated.	Observed.	Ramsay and Young.
$C_6H_5F$ .....	.....	....	.....	2.43	.....
$C_6H_5Cl$ .....	1.1246	262	2.34	2.34-2.45	.....
$C_6H_5Br$ .....	1.1802	275	1.76	.....	.....
$C_6H_5I$ .....	1.2772	298	1.47	.....	.....
$C_6H_5$ .....	.944	220	2.83	2.82	.....
$CCl_4$ .....	1.010	235	1.53	.....	.....
$SnCl_4$ .....	1.290	301	1.16	.....	.....
$(C_2H_5)_2O$ .....	1.047	244	3.30	.....	4.06
$CH_3OH$ .....	.440	103	3.21	.....	3.7
$C_2H_5OH$ .....	.620	144	3.15	.....	3.5
$C_2H_5OH$ .....	.800	186	3.11	.....	3.6
$CH_3COOH$ ...	.630	147	2.45	2.46	.....

It will be seen that the values for benzene and acetic acid, calculated from the mean ratios, agree very well with those directly observed, and this may be taken as evidence in favour of the accuracy of the method of direct measurement adopted. On the other hand, the calculated values for ether and the alcohols are considerably lower than those previously given by Ramsay and myself. But it may be pointed out that the critical temperature of ether was almost certainly slightly underestimated, owing to the employment of the vapour of methyl salicylate as a jacket. There is no reason to suspect any error in the determination of the critical pressure; and if the constants for Biot's formula be taken as correct, the calculated temperature corresponding to the critical pressure would be 194.4 instead of 193.8, and the higher value agrees well with a more recent determination by Ramsay, who in this case employed the vapour of quinoline as a jacket. The correction of the critical temperature of ether would give a lower value to the critical volume.

Again, Professor Tait has recently made an exhaustive mathematical investigation of the relations of pressure, temperature, and volume of several substances, including ether,

and he has pointed out that the critical temperature is probably a little higher than 193·8, and that the critical volume of this substance is certainly lower than 4 cubic centim., and is more probably about 3·5 cubic centim., a value that agrees fairly well with that calculated by the method described.

In the case of the alcohols the critical volumes given by Ramsay and myself were estimated by inspection of the curves representing the relation of the specific gravities of liquid and saturated vapour to the temperature, and of the specific volumes to the pressures, and they were admittedly only approximate values.

M. Guye has shown (*Comptes Rendus*, cxii. p. 1257) that an approximate relation exists between the critical temperature, pressure, and volume of a substance and its theoretical vapour-density compared with air. This is expressed by the equations

$$d = 1146 \frac{\delta\theta}{\pi(1070 + \theta)} = \frac{M}{28\cdot87};$$

where  $\delta$  is the specific gravity at the critical point compared with water at 4°,  $\theta$  the absolute critical temperature,  $\pi$  the critical pressure, and  $M$  the molecular weight. The critical volumes of ether and the alcohols previously given by Ramsay and myself are certainly in better agreement with this relation than those which I now find; but it may be mentioned that, with the exception of iodobenzene, all the substances referred to in this paper give somewhat higher values of  $d$  than the quotient  $\frac{M}{28\cdot87}$  if the molecular volumes in

Table XXII. be taken as correct.

It may, I think, be safely stated that the true critical volumes are not lower than those directly observed, but it is possible that they may be a little higher. It is therefore perhaps too much to say that the values given in the table are definitely established, but I am inclined to think that they may be accepted as fairly close approximations to the truth.

If that is so, it would appear from Table XVII. that *the ratio of the actual critical density to the theoretical density is for very many substances about 4·4*. Ethyl and propyl alcohol give somewhat higher values, while for methyl alcohol and acetic acid, especially the latter, the ratios are extremely high.

XVII. *The Construction of Non-Inductive Resistances.*By Prof. W. E. AYRTON, *F.R.S.*, and T. MATHER\*.

[Plate IV.]

WITH all electric methods devised for measuring the power given by a varying current to a circuit that may possess inductance or capacity it is necessary to employ a resistance which shall have zero inductance, consequently it is important to consider how such resistances may most easily be made.

If the inductance of this nominally non-inductive resistance be not zero, the error thus introduced into the measurement can still be made relatively unimportant if the time-constant of this portion of the circuit be made small. For, as shown by Dr. Sumpner and one of us, in a paper† read before this Society on June 12th of this year, the following proportion holds true in all the nine methods of measuring power there considered:—

$$\frac{\text{the watts as measured}}{\text{the true watts}} = \frac{1 + \tan \theta \cdot \tan \phi}{1 + \tan^2 \phi},$$

where  $\theta$  and  $\phi$  are the angles of phase-difference between the current and the P.D. for the circuit the power given to which we desire to measure, and for the auxiliary circuit respectively.

Now for any given configuration of a circuit, the time-constant will be the smaller the higher the specific resistance of the conductive material; hence it is very desirable to use a material of high specific resistance, like carbon. For this reason, glow-lamps constitute valuable small time-constant resistances, but carbon has the disadvantage that its resistance varies rapidly with temperature. Hence, since with the methods of measuring power referred to it is necessary to know the resistance of the non-inductive circuit at the moment of making the measurement, it follows that if carbon be employed an extra measurement has to be made.

When the non-inductive resistance is put in series with the circuit the power given to which we desire to measure, as, for example, with the three-voltmeter method of measuring power, a measurement of the resistance of the glow-lamps merely means the reading of an extra instrument at the moment the power-test is made; but when the two circuits are joined in parallel, as, for example, with the one-voltmeter and two-ammeter method of measuring power, a measurement of the

\* Communicated by the Physical Society: read June 26, 1891.

† "Alternate Current and Potential Difference Analogies in the Methods of Measuring Power," *Phil. Mag.* August 1891, p. 204.



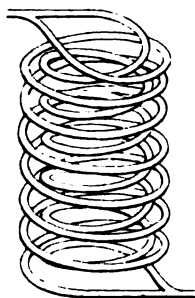


Fig. 2.

*Right and Left Handed  
Spirals in Parallel.  
Opposing one another.*

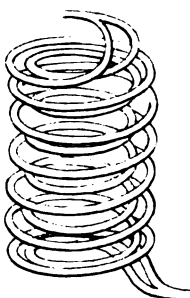


Fig. 4.

*Two Right Handed Spirals  
in Parallel, Assisting one  
another.*

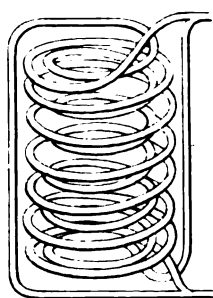


Fig. 5.

*Two Right Handed Spirals  
in Parallel, Opposing one  
another.*

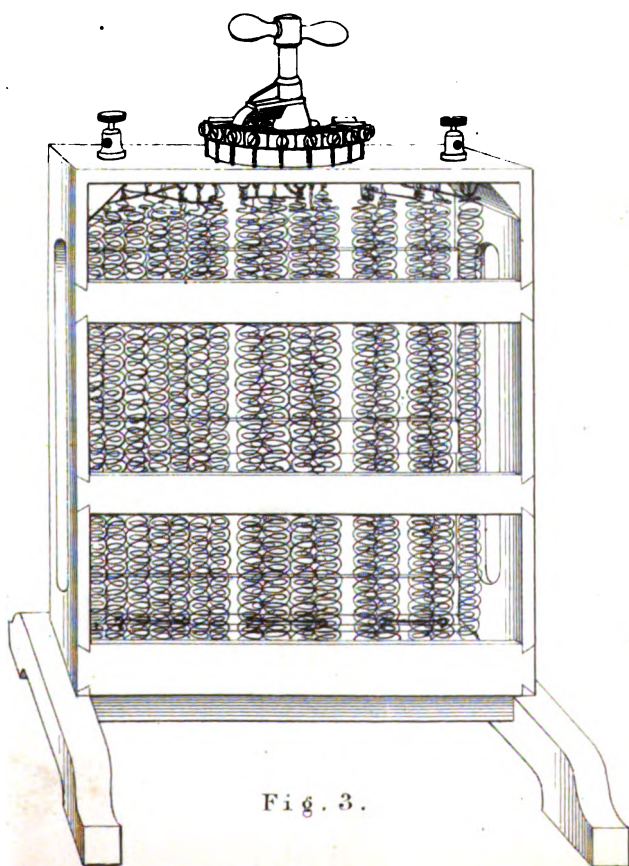


Fig. 3.



resistance of the glow-lamps cannot be made simultaneously with the power-test, since to do this would require the introduction of an ammeter, and therefore of inductance, into the circuit, which should be non-inductive.

Further, carbon is unsuitable for portable resistances on account of its brittle nature. Platinoid, on the other hand, is flexible, has a low temperature-coefficient, and a high specific resistance, though not of course nearly as high as that possessed by carbon. Platinoid therefore appeared to us to be the best material to employ in the construction of non-inductive resistances to be used for power-tests.

It is well known that a wire doubled on itself has a very small inductance, which approximates to 3.77 times the total length of the wire in centimetres as the parts approach each other. This value can, as Maxwell pointed out, be reduced by using flat strips instead of round wires; and, if the strips be bare and be placed vertically, it is clear that the cooling action will be considerable, so that relatively strong currents will produce but little rise in temperature or increase of resistance.

We therefore decided in 1887 to construct the non-inductive resistance seen in fig. 1, Plate IV., consisting of twelve platinoid strips, each 6 metres long, 4 centim. wide, and 0.25 millim. thick. Each strip is doubled on itself, two layers of carefully shell-lacqued silk, 0.075 millim. thick, being inserted between the front and back portions. The whole is bound together by means of a narrow silk ribbon wrapped round spirally, considerable gaps being left between the spires of the silk ribbon so that the platinoid should have plenty of free surface for cooling.

For the purpose of expelling moisture from the silk and the shell-lac varnish, when the resistance-strips are first put up, a current was passed through each strip strong enough to make it fairly hot. During this heating frequent short-circuitings occurred from rough points of the metal piercing the silk, a single layer only of which was originally employed to separate the front and back portions. An additional layer of silk was therefore inserted. Trouble was also experienced from the rough edges of the metal causing short-circuits; but by cutting the silk wider than the metal and by folding the edge of the silk over the edge of the platinoid strip, this difficulty was overcome.

The doubled strips are permanently joined up in sets of three, and to the ends of each set are soldered mercury-cups and binding-screws. The four sets of three can be joined up in series, or in parallel, or in parallel-series by bridge-pieces

dipping into the mercury-cups, and, when all are in series, the resistance of the 72 metres of strip at  $15^{\circ}$  C. is 2.932 ohms. The resistance of the arrangement does not alter by more than one tenth per cent. when a current of 15 amperes is passing through each strip.

The wooden frame which carries this series of platinoid strips hangs on paraffined ebonite pegs attached to one of the laboratory walls, so that it is well insulated.

The inductance of the set of strips, even when all are in series, is so small that we have not been able to measure it even with the secohmmeter. Some of the tests have given indications of a small negative result, which, if true, would mean that the capacity-effect slightly overbalanced the inductance; but a calculation, which we have made, appears to show that with the dimensions in question such a result is impossible. We can therefore only conclude that this resistance-frame, which was constructed by two of our former students, Messrs. C. G. Lamb and E. W. Smith, fulfils the object for which it was intended so well that the inductance cannot be detected with certainty by any test that we have hitherto tried. We therefore have decided to duplicate the arrangement, the wooden framework (only one half of which is seen in fig. 1) having been constructed large enough to hold a second set of strips.

Another method of constructing non-inductive resistances for large currents, which has been in use at the Central Institution for the past eighteen months, is illustrated in fig. 2, and consists in winding two bare platinoid wires of equal length and thickness into two spirals, one right-handed, the other left-handed, the diameters of the two spirals differing slightly from each other so that one spiral can be placed inside the other. They are then connected up in parallel, so that when a current is sent through them it circulates clockwise round one spiral and counterclockwise round the other, the magnetic effects of the two thus tending to neutralize one another and to produce a combination with small inductance.

The inductance of coils constructed in this way is almost as small as if the wires were doubly wound like an ordinary resistance-coil, *but they possess the great advantage that parts differing much in potential are not close to one another.* The wires therefore require no insulating covering, for no harm will occur if one spiral accidentally touches the other, provided that reasonable care has been taken to space the convolutions fairly uniformly. Further, as the cooling surface, for a given total cross section of the conductor, is much greater for two concentric spirals than for a single spiral of

thicker wire, it follows that this method of constructing a resistance not only greatly reduces the inductance, but also enables a much larger current to be carried for a given variation of resistance produced by the current. Hence for a given current and for a given permissible rise of temperature finer wire can be used; the coils can therefore be made shorter, and the inductance for this reason still further lessened.

Lastly, even when such right- and left-handed spirals are traversed by a direct current, much less disturbance is produced in a neighbouring delicate galvanometer than if a singly-wound spiral resistance be employed; so that these right- and left-handed spirals of bare wire are valuable in the construction of resistance-frames for large direct as well as for large alternating currents.

A number of portable resistance-coils have been constructed in this way for general use in the laboratories of the Central Institution. One of these is seen in fig. 3. It has also been found convenient to fit up a number of stationary right- and left-handed concentric spirals of platinoid in the dynamo laboratory, for use in the regular experiments with alternate currents.

Table I. gives the particulars of some portable sets of stand coils in the laboratories of the Central Institution, the second three of which have been composed of right- and left-handed spirals in the way just described and illustrated in fig. 3.

TABLE I.  
Particulars of Portable Stand Coils.

Mark on the Stand.	Resistance, in Ohms.	Number of Spirals in the Set.	Length of each Spiral.	Number of Convolutions in each Spiral.		Outside diameter of the Convolutions.		Size of the Wire (S.W.G.).
1 .....	1.8	6	inches. $18\frac{3}{4}$	78		inches. $1\frac{1}{8}$		No. 12
2 .....	2.54	12	$16\frac{1}{4}$	63		$1\frac{1}{4}$		No. 10
3 .....	8.59	12	$16\frac{1}{4}$	84		$1\frac{1}{4}$		No. 13
				Outer.	Inner.	Outer.	Inner.	
4 .....	1.4	{ 20 double, that is 40 coils in all. }	$16\frac{1}{4}$	15	21	inches. $1\frac{1}{8}$	inches. $\frac{7}{8}$	No. 13
5 .....	5.0		$16\frac{1}{4}$	27	37	$1\frac{1}{8}$	$\frac{1}{4}$	No. 15 $\frac{1}{2}$
6 .....	99		17	54	79	$\frac{3}{4}$	$\frac{1}{2}$	No. 27

Table II. gives the results of experiments made on the sets marked 2, 3, 4, 5, 6 by means of the secohmmeter; the set marked 6 being tested when each pair of coils were joined up in parallel so as to increase the inductance as well as when joined up so as to diminish it.

TABLE II.  
Portable Platinoid Spiral Resistances (fig. 3).

Mark on the Stand.	Winding.	Resistance, in Ohms.	Inductance, in Secohms.	Time-constant, in Seconds.
2 ...	Set of Singly-Wound Spirals ...	2.54	0.000059	$23 \times 10^{-6}$
3 ...	Set of Single-Wound Spirals ...	8.59	0.00015	$18 \times 10^{-6}$
6 {	Set of Doubly-Wound Spirals; Current circulating in all in the Same Direction .....	98.1	0.0021	$21 \times 10^{-6}$
6 {	Same set of Doubly-Wound Spirals; Current circulating in Opposite Directions.....	99	0.00013	$1.3 \times 10^{-6}$
4 {	Set of Doubly-Wound Spirals; Current circulating in Opposite Directions .....	1.4	0.000004	$2.8 \times 10^{-6}$
5 {	Set of Doubly-Wound Spirals; Current circulating in Opposite Directions .....	5.0	0.0000094	$1.9 \times 10^{-6}$

The mean time-constant, therefore, of one of our sets of spirals, whether singly-wound or doubly-wound, provided that the current circulates in all the convolutions in the same direction, is about  $21 \times 10^{-6}$ ; whereas if the spirals be doubly-wound and the current be circulating in opposite directions in the two sets of spirals, the mean time-constant is about  $2 \times 10^{-6}$ , or about one tenth of the preceding.

As there happens to be in the laboratory a solenoid, the silk-covered copper wire on which is wound in a series of concentric sections, it was thought interesting to compare the time-constant of two of the sections joined up in parallel, when the current circulated round both in the same direction, with the time-constant when it circulated in opposite directions. Figs. 4 and 5, Plate IV., show the direction of the current in the two cases.

	Resistance, in Ohms.	Self-induction, in Secohms.	Time-constant in Seconds.
Currents flowing round both coils in the same direction (fig. 4) ...	0.346	0.00059	$17 \times 10^{-6}$
Currents flowing round the coils in the opposite direction (fig. 5) ...	0.346	0.000024	$0.69 \times 10^{-6}$

The self-induction and time-constant have therefore been reduced to one twenty-fourth part by sending the currents in opposite directions round the two, but the method of winding shown in fig. 5 could not, of course, be employed with the non-inductive resistances constructed of bare wire for large currents described in this communication ; since the fundamental condition—that *parts differing much in potential should not be near one another*—would not be fulfilled.

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XVIII. *A Theory concerning the Constitution of Matter.*

By CHARLES V. BURTON, D.Sc.\*

THE theory described in the following pages is based essentially on one fundamental hypothesis ; without the aid of any further assumptions, equations of motion can be deduced, and these, when simplified by certain conditions of symmetry, lead at once to Newton's Laws. In dealing—vaguely enough—with other problems, such as gravitation and the discrete nature of atoms, it is found necessary to make further limitations ; and a few suggestions are also made whose nature is purely speculative. But there remains the one central idea, whose development is the especial object of this paper, and in the concluding paragraphs the doctrine will be stated in its most general form and the arguments once more briefly enumerated.

1. Space, so far as we know it, is filled with a medium, whose ultimate nature may be fluid, but which, owing to turbulent motion or some other cause, has elastic properties resembling in some respects those of a solid. The resistance offered by such a medium to the motion of material bodies presents a problem of some difficulty, *so long as we suppose an atom to consist always of the same portion of æthereal or other substance*; but further on it will be shown that, with a different assumption, the question may assume a new aspect. Before leaving this subject, however, I may point out what appears to me a very serious difficulty of the present view : a perfect vacuum is (at least very nearly) a perfect insulator, and air also insulates well, so that the æther surrounding an electrically charged terrestrial body may remain in a state of stress for a considerable period without appreciable progressive yielding, while at the same time this charged body is being whirled through the æther, which continually gives way like an almost perfect liquid.

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2. *Fundamental Assumption. Strain-Figure.*—Consider a region, either infinite or having very distant boundaries, and filled with a homogeneous isotropic elastic medium, whose condition throughout is one of stable equilibrium for small strains of any type. Let the medium now be strained, and held in its strained condition by some compelling agency: there will be a corresponding distribution of stress in the medium, and, provided the strain has at no point too great a value, the original condition will be completely regained after the compelling agency has been removed. But suppose that, instead, the medium is strained further and further from its initial state, and suppose that the restoring stresses do not always increase with the strain, but that beyond a certain point in the process they begin to fall off in value, until at last a point is reached at which the general tendency of the stress is to further increase the strain. If the compelling agency is now withdrawn, the medium will subside into a new condition of stable equilibrium, involving stress and strain at every point. The state of things thus impressed on the medium is, according to my view, an atom or a constituent of an atom; it will hereafter be referred to as a “*strain-figure*,” and we may now proceed to examine its dynamical properties.

3. *Rigid Body Displacements.*—A strain-figure, being of itself in equilibrium, will remain in equilibrium if transferred to some other portion of the medium, or if its orientation with respect to the medium is changed (for originally the medium was homogeneous and isotropic); we may therefore give to the strain-figure any displacement of which a rigid body would be capable, and the resulting condition of the medium will be one of equilibrium; there is no statical resistance to such displacement, and no question of the medium giving way.

4. *Equations of Motion.*—If a strain-figure is in motion through the medium, certain conditions must be satisfied in order that its degrees of freedom may not be more than those of a rigid body; in order, that is, that the strain-figure may retain the same form as if it were at rest in the medium. For suppose that disturbances of the same type as the strains in the strain-figure are propagated through the medium with velocity  $V$ ; then obviously a necessary condition is that the translational velocity of the strain-figure must be very small compared with  $V$ , the rotational motion being (in general) subject to a similar restriction, which cannot be quite so simply expressed. If  $V$  is (as I imagine) the velocity with which gravitation is propagated, it is a quantity whose finiteness has not yet been demonstrated, and compared with which all known molar and molecular motions are extremely slow.

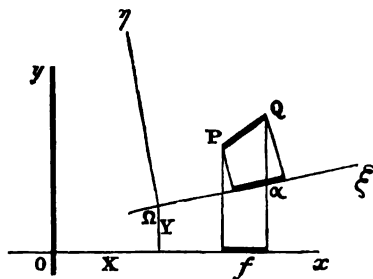


Another condition to be fulfilled by the motion of the strain-figure is this: the acceleration must be very small compared with  $V/T$ , where  $V/T$  is the radius of the smallest spherical surface within which the whole appreciable *effective mass* (17 a) of the strain-figure may be considered to reside.

Assuming, then, that the necessary conditions are satisfied, and that the strain-figure has only six degrees of freedom, let us choose three rectangular axes (those of  $\xi, \eta, \zeta$ , with origin  $\Omega$ ) fixed in the strain-figure, and three other rectangular axes (those of  $x, y, z$ , with origin  $O$ ) fixed in the medium and in space; let the coordinates of  $\Omega$  referred to  $Ox, Oy, Oz$  be  $(X, Y, Z)$ , and let the direction-cosines of the  $\xi, \eta, \zeta$  axes be given by the scheme

	$x-X$	$y-Y$	$z-Z$	
$\xi$	$l_1$	$m_1$	$n_1$	
$\eta$	$l_2$	$m_2$	$n_2$	$\dots \dots (1)$
$\zeta$	$l_3$	$m_3$	$n_3$	

(For convenience the diagram is only drawn in two dimensions.)



Let  $P(\xi, \eta, \zeta)$  be the *undisturbed* position of a certain volume-element of æther (that is, the position which this element would occupy if the strain-figure were non-existent), and let  $Q(\xi + \alpha, \eta + \beta, \zeta + \gamma)$  be the *actual* position of the same element. Then, in accordance with the geometrical conditions of motion,

$$\alpha, \beta, \gamma \text{ are functions of } \xi, \eta, \zeta \text{ only ; } \dots \dots (2)$$

they are the components of displacement of the element whose undisturbed position would have been  $\xi, \eta, \zeta$ .

If the components of  $PQ$  parallel to  $Ox, Oy, Oz$  be called  $f, g, h$  respectively, we shall have, after the manner of (1), the scheme

	$f$	$g$	$h$	
$\alpha$	$l_1$	$m_1$	$n_1$	
$\beta$	$l_2$	$m_2$	$n_2$	. . . . . (3)
$\gamma$	$l_3$	$m_3$	$n_3$	

Let the *original* density of the æther be taken as unity; and consider that portion of æther which, in the *undisturbed* condition of the medium, would have filled the volume-element  $d\xi d\eta d\zeta$  with coordinates  $(\xi, \eta, \zeta)$ . Since  $f, g, h$  are the displacements parallel to  $Ox, Oy, Oz$ , of the portion of æther so defined,  $\dot{f}, \dot{g}, \dot{h}$  will be the actual velocity-components of this portion, and the energy due to the motion of the strain-figure is

$$T = \frac{1}{2} \iiint (\dot{f}^2 + \dot{g}^2 + \dot{h}^2) d\xi d\eta d\zeta. \quad (4)$$

Now let the axes  $\Omega\xi, \Omega\eta, \Omega\zeta$  be instantaneously coincident in direction with  $Ox, Oy, Oz$  respectively, so that

$$l_1 = m_2 = n_3 = 1; \quad l_2 = l_3 = m_3 = m_1 = n_1 = n_2 = 0, \quad (5)$$

and

$$\dot{l}_1 = \dot{m}_2 = \dot{n}_3 = 0; \quad \dot{n}_2 = -\dot{m}_3 = \omega_1; \quad \dot{l}_3 = -\dot{n}_1 = \omega_2; \quad \dot{m}_1 = -\dot{l}_2 = \omega_3, \quad (6)$$

where  $\omega_1, \omega_2, \omega_3$  are the angular velocity-components of the strain-figure about the axes of  $\xi, \eta, \zeta$  or of  $x, y, z$ ; relations which, in general, are only instantaneously true.

From (3),

$$\dot{f} = l_1\dot{\alpha} + l_2\dot{\beta} + l_3\dot{\gamma} + \dot{l}_1\alpha + \dot{l}_2\beta + \dot{l}_3\gamma;$$

and writing

$$\frac{\partial \alpha}{\partial \xi} \equiv \alpha_1; \quad \frac{\partial \alpha}{\partial \eta} \equiv \alpha_2; \quad \frac{\partial \alpha}{\partial \zeta} \equiv \alpha_3; \quad \&c., \quad (7)$$

the last equation becomes

$$\begin{aligned} \dot{f} = & l_1(\alpha_1\dot{\xi} + \alpha_2\dot{\eta} + \alpha_3\dot{\zeta}) + l_2(\beta_1\dot{\xi} + \beta_2\dot{\eta} + \beta_3\dot{\zeta}) + l_3(\gamma_1\dot{\xi} + \gamma_2\dot{\eta} + \gamma_3\dot{\zeta}) \\ & + \dot{l}_1\alpha + \dot{l}_2\beta + \dot{l}_3\gamma. \end{aligned} \quad (8)$$

Again, from (1),

$$\xi = l_1(x - X) + m_1(y - Y) + n_1(z - Z),$$

so that

$$\begin{aligned} \dot{\xi} = & \dot{l}_1(l_1\xi + l_2\eta + l_3\zeta) + \dot{m}_1(m_1\xi + m_2\eta + m_3\zeta) + \dot{n}_1(n_1\xi + n_2\eta + n_3\zeta) \\ & - l_1\dot{X} - m_1\dot{Y} - n_1\dot{Z}; \end{aligned}$$

or, using (5) and (6),

$$\left. \begin{aligned} \dot{\xi} &= \omega_3\eta - \omega_2\zeta - \dot{X}, \\ \dot{\eta} &= \omega_1\zeta - \omega_3\xi - \dot{Y}, \\ \dot{\zeta} &= \omega_2\xi - \omega_1\eta - \dot{Z}. \end{aligned} \right\}$$

Similarly  
and

Substituting these values in (8), and again using (5) and (6), we obtain

$$\left. \begin{aligned} \dot{f} &= -\alpha_1 \dot{X} - \alpha_2 \dot{Y} - \alpha_3 \dot{Z} + \omega_1(\alpha_2 \zeta - \alpha_3 \eta) + \omega_2(\alpha_3 \xi - \alpha_1 \zeta + \gamma) \\ &\quad + \omega_3(\alpha_1 \eta - \alpha_2 \xi - \beta). \\ \text{Similarly} \\ \dot{g} &= -\beta_1 \dot{X} - \beta_2 \dot{Y} - \beta_3 \dot{Z} + \omega_1(\beta_2 \zeta - \beta_3 \eta - \gamma) + \omega_2(\beta_3 \xi - \beta_1 \zeta) \\ &\quad + \omega_3(\beta_1 \eta - \beta_2 \xi + \alpha), \\ \text{and} \\ \dot{h} &= -\gamma_1 \dot{X} - \gamma_2 \dot{Y} - \gamma_3 \dot{Z} + \omega_1(\gamma_2 \zeta - \gamma_3 \eta + \beta) + \omega_2(\gamma_3 \xi - \gamma_1 \zeta - \alpha) \\ &\quad + \omega_3(\gamma_1 \eta - \gamma_2 \xi). \end{aligned} \right\} \quad (9)$$

If these values are substituted in (4), we obtain immediately a complete expression for the energy due to the motion of the strain-figure; and this expression involves only  $\dot{X}$ ,  $\dot{Y}$ ,  $\dot{Z}$ ,  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ , and quantities which remain constant throughout the motion. We may therefore apply the principle of moving axes to find the components F, G, H of effective force on the strain-figure; thus

$$F = \frac{d}{dt} \frac{\partial T}{\partial \dot{X}} - \omega_3 \frac{\partial T}{\partial \dot{Y}} + \omega_2 \frac{\partial T}{\partial \dot{Z}},$$

which by means of (4) and (9) becomes

$$\begin{aligned} F &= (11)\dot{X} + (12)\dot{Y} + (31)\dot{Z} \\ &\quad - (12)\omega_3 \dot{X} - (22)\omega_3 \dot{Y} - (23)\omega_3 \dot{Z} \\ &\quad + (31)\omega_2 \dot{X} + (23)\omega_2 \dot{Y} + (33)\omega_2 \dot{Z} \\ &\quad + \{(31\eta) - (12\zeta) + (\beta_1\gamma)\}\dot{\omega}_1 + \{(11\zeta) - (31\xi) + (\gamma_1\alpha)\}\dot{\omega}_2 \\ &\quad + \{(12\xi) - (11\eta) + (\alpha_1\beta)\}\dot{\omega}_3 \\ &\quad + \{(31\zeta) - (33\xi) + (\gamma_3\alpha)\}\omega_2^2 + \{(12\eta) - (22\xi) - (\alpha_2\beta)\}\omega_3^2 \\ &\quad + \{2(23\xi) - (12\zeta) - (31\eta) + (\alpha_3\beta) - (\gamma_2\alpha)\}\omega_2\omega_3 \\ &\quad + \{(22\zeta) - (23\eta) + (\beta_2\gamma)\}\omega_3\omega_1 + \{(33\eta) - (23\zeta) + (\beta_3\gamma)\}\omega_1\omega_2, \end{aligned} \quad (10)$$

with similar values for G and H, where we write

$$\left. \begin{aligned} \iiint (\alpha_1^2 + \beta_1^2 + \gamma_1^2) d\xi d\eta d\zeta &\equiv (11), \text{ \&c.,} \\ \iiint (\alpha_2\alpha_3 + \beta_2\beta_3 + \gamma_2\gamma_3) d\xi d\eta d\zeta &\equiv (23) \equiv (32), \text{ \&c.,} \\ \iiint (\alpha_2\alpha_3 + \beta_2\beta_3 + \gamma_2\gamma_3)\xi d\xi d\eta d\zeta &\equiv (23\xi) \equiv (32\xi), \text{ \&c.,} \\ \iiint (\beta_1\gamma - \gamma_1\beta) d\xi d\eta d\zeta &\equiv (\beta_1\gamma) \equiv -(\gamma_1\beta), \text{ \&c.} \end{aligned} \right\} \quad (11)$$

Again, if L, M, N are the effective couples,

$$\begin{aligned}
 L = & \frac{d}{dt} \cdot \frac{\partial T}{\partial \omega_1} - \dot{Z} \frac{\partial T}{\partial \dot{Y}} + \dot{Y} \frac{\partial T}{\partial \dot{X}} - \omega_3 \frac{\partial T}{\partial \omega_2} + \omega_2 \frac{\partial T}{\partial \omega_3} \\
 = & \{ (12\zeta) - (31\eta) - (\beta 1\gamma) \} \ddot{X} + \{ (23\eta) - (22\zeta) + (\beta 2\gamma) \} \ddot{Y} \\
 & + \{ (33\eta) - (23\zeta) + (\beta 3\gamma) \} \ddot{Z} \\
 & + (23) \dot{Y}^2 - (23) \dot{Z}^2 + \{ (33) - (22) \} \dot{Y} \dot{Z} - (12) \dot{Z} \dot{X} + (31) \dot{X} \dot{Y} \\
 & + \{ (12\xi) - (11\eta) + (\alpha 1\beta) \} \omega_2 \dot{X} + \{ (31\xi) - (11\zeta) - (\gamma 1\alpha) \} \omega_3 \dot{X} \\
 & + \{ (33\eta) - (23\zeta) + (\beta 3\gamma) \} \omega_1 \dot{Y} + \{ (22\zeta) - (23\eta) - (\beta 2\gamma) \} \omega_1 \dot{Z} \\
 & + \{ (22\xi) - (33\xi) + (31\zeta) - (12\eta) + (\gamma 3\alpha) + (\alpha 2\beta) \} (\omega_2 \dot{Y} - \omega_3 \dot{Z}) \\
 & + \{ 2(23\xi) - (12\zeta) - (31\eta) + (\alpha 3\beta) - (\gamma 2\alpha) \} (\omega_3 \dot{Y} + \omega_2 \dot{Z}) \\
 & + \{ (22\zeta^2) + (33\eta^2) - 2(23\eta\zeta) - (\beta 2\gamma\zeta) + (\beta 3\gamma\eta) \} \dot{\omega}_1 \\
 & + \{ (23\zeta\xi) + (31\eta\zeta) - (33\xi\eta) - (12\zeta^2) - (\gamma 2\alpha\zeta) + (\gamma 3\alpha\eta) \\
 & \quad - (\beta 3\gamma\xi) + (\beta 1\gamma\zeta) \} \dot{\omega}_2 \\
 & + \{ (12\eta\zeta) + (23\xi\eta) - (22\zeta\xi) - (31\eta^2) - (\alpha 2\beta\zeta) + (\alpha 3\beta\eta) \\
 & \quad - (\beta 1\gamma\eta) + (\beta 2\gamma\xi) \} \dot{\omega}_3 \\
 & + \{ (\alpha 3\beta\xi) - (\alpha 1\beta\zeta) + (\gamma 1\alpha\eta) - (\gamma 2\alpha\xi) + (\beta\gamma) \} (\omega_3^2 - \omega_2^2) \\
 & + \{ \alpha 2\beta\xi - (\alpha 1\beta\eta) + (\gamma 3\alpha\xi) - (\gamma 1\alpha\zeta) + (\beta^2) - (\gamma^2) \} \omega_2 \omega_3 \\
 & + \{ (33\xi\eta) + (12\zeta^2) - (23\zeta\xi) - (31\eta\zeta) + (\gamma 2\alpha\zeta) - (\gamma 3\alpha\eta) \\
 & \quad + (\beta 3\gamma\xi) - (\beta 1\gamma\zeta) \} \omega_2 \omega_1 \\
 & + \{ (12\eta\zeta) + (23\xi\eta) - (22\zeta\xi) - (31\eta^2) - (\alpha 2\beta\zeta) + (\alpha 3\beta\eta) \\
 & \quad - (\beta 1\gamma\eta) + (\beta 2\gamma\xi) \} \omega_1 \omega_3, \quad \dots \quad (12)
 \end{aligned}$$

with similar values for M and N, where, in addition to (11), we have

$$\left. \begin{aligned}
 \iiint (\alpha_1 \alpha_2 + \beta_1 \beta_2 + \gamma_1 \gamma_2) \eta \zeta \, d\xi \, d\eta \, d\zeta &\equiv (12\eta\zeta) \text{ \&c.}, \\
 \iiint (\beta_1 \gamma - \gamma_1 \beta) \xi \, d\xi \, d\eta \, d\zeta &\equiv (\beta 1\gamma\zeta) \text{ \&c.}, \\
 \iiint \beta \gamma \, d\xi \, d\eta \, d\zeta &\equiv (\beta\gamma) \text{ \&c.}
 \end{aligned} \right\} \quad (13)$$

Mr. G. H. Bryan has pointed out to me that the equations of motion (10) and (12) are of exactly the *same form* as those of a solid immersed in a perfect liquid.

5. If U is the force-function of the impressed forces, we shall have of course

$$F = \frac{\partial U}{\partial X}, \quad G = \frac{\partial U}{\partial Y}, \quad H = \frac{\partial U}{\partial Z};$$

and evidently

$$\frac{\partial U}{\partial X} = \iiint \left( a \frac{\partial f}{\partial X} + b \frac{\partial g}{\partial X} + c \frac{\partial h}{\partial X} \right) d\xi' d\eta' d\zeta';$$

where  $d\xi' d\eta' d\zeta'$  is a volume-element in the *actual* condition of the medium,  $f, g, h$  the displacements of the æther which now fills this volume-element, and  $a d\xi' d\eta' d\zeta'$  &c., the forces exerted on the element of æther. Remembering (1), (3), (5), and (7), we may write the last equation

$$\frac{\partial U}{\partial X} = -\iiint (a\alpha_1 + b\beta_1 + c\gamma_1) d\xi' d\eta' d\zeta'; \quad . \quad . \quad (14)$$

$\frac{\partial U}{\partial Y}$  and  $\frac{\partial U}{\partial Z}$  having similar values, and  $\frac{\partial U}{\partial \theta_1}$  &c. being similarly obtainable.

We may also express  $a, b, c$  in terms of the components of stress  $[\xi\xi], [\eta\xi]$  &c.; thus

$$\left. \begin{aligned} a &= -\frac{\partial}{\partial \xi} [\xi\xi] - \frac{\partial}{\partial \eta} [\eta\xi] - \frac{\partial}{\partial \zeta} [\zeta\xi], \\ b &= -\frac{\partial}{\partial \xi} [\xi\eta] - \frac{\partial}{\partial \eta} [\eta\eta] - \frac{\partial}{\partial \zeta} [\zeta\eta], \\ c &= -\frac{\partial}{\partial \xi} [\xi\zeta] - \frac{\partial}{\partial \eta} [\eta\zeta] - \frac{\partial}{\partial \zeta} [\zeta\zeta]. \end{aligned} \right\} \quad . \quad . \quad (15)$$

In this section it has been virtually assumed that the strain-figure is exactly superimposed on the otherwise existing condition of the medium.

6. If the motion of the strain-figure is one of pure translation,  $\omega_1, \omega_2, \omega_3$  are all constantly zero, and equation (10) reduces to

$$\left. \begin{aligned} F &= (11)\ddot{X} + (12)\ddot{Y} + (31)\ddot{Z}; \\ G &= (12)\ddot{X} + (22)\ddot{Y} + (23)\ddot{Z}; \\ H &= (31)\ddot{X} + (23)\ddot{Y} + (33)\ddot{Z}; \end{aligned} \right\} \quad \text{at the same time} \quad . \quad (16)$$

Now construct the ellipsoid

$$(11)\xi^2 + (22)\eta^2 + (33)\zeta^2 + 2(23)\eta\zeta + 2(31)\zeta\xi + 2(12)\xi\eta = M\epsilon^2; \quad (17)$$

and it is evident from (16) above that when the motion is one of pure translation, the effective force (components  $F, G,$

H) is perpendicular to the diametral plane of the acceleration (components  $\ddot{X}$ ,  $\ddot{Y}$ ,  $\ddot{Z}$ ), taken with respect to the ellipsoid (17).

(11), (22), (33), which are the sums of squares, are the values of the effective mass in the directions of the axes of reference; while (23), (31), (12), which are the sums of products, correspond to products of inertia in Rigid Dynamics, and may be called "products of mass." It may easily be shown that if  $r$  is the length of any given radius of the ellipsoid (17), the effective mass reckoned in the direction of this radius is  $M\epsilon^2/r^2$ . It may also be remarked that even when the motion is one of pure translation, there will in general be finite effective couples, as is immediately evident from (12).

7. *Case of Symmetry.*—Consider now the particular case in which the strain-figure is symmetrical about a point, and let this point be  $\Omega$ , the origin of the axes of  $\xi$ ,  $\eta$ ,  $\zeta$ . We shall then have

$$\left. \begin{aligned} (11) &= (22) = (33) = \text{effective mass}; \\ (23) &= (31) = (12) = 0. \end{aligned} \right\} \quad (17a)$$

It is also evident that a rotation of the strain-figure about any axis through its centre of symmetry corresponds to no physical change whatever; there is no possibility of such rotation, nor can any influence exerted on the medium have a tendency to turn the strain-figure about its centre of symmetry. Hence a strain-figure symmetrical about a point is dynamically equivalent to a single particle of mass

$$\begin{aligned} \iiint (\alpha_1^2 + \beta_1^2 + \gamma_1^2) d\xi d\eta d\zeta &= \iiint (\alpha_2^2 + \beta_2^2 + \gamma_2^2) d\xi d\eta d\zeta \\ &= \iiint (\alpha_3^2 + \beta_3^2 + \gamma_3^2) d\xi d\eta d\zeta \end{aligned}$$

placed at its centre of symmetry.

It is worth remarking that the theory now considered, though differing so widely from the theory of Boscovich, leads to the same dynamical results.

8. So far we have only considered the case of a single strain-figure. When there are more than one, the experimental properties of matter lead us to suppose:—

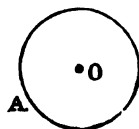
(i) That the entire distribution of displacement in the medium is to be found (at least very approximately) by compounding geometrically the distributions which the various strain-figures would have produced separately.

(ii) That the strain-figures exert forces upon one another, thus changing or tending to change their motion through the medium.

In speaking of the medium I have more particularly in mind the hypothesis of a turbulently moving liquid, as propounded by Sir W. Thomson\* and modified by Prof. Fitzgerald†. Without entering on the subject mathematically (which I am unable to do), it may be noticed that, according to this view, the æther is made up of interlacing vortex-filaments, the interspaces between which are filled with quiescent or irrotationally moving liquid. The network of filaments is equivalent to a sponge-like compressible solid, whose pores, however, are completely filled with incompressible fluid. The medium, *taken as a whole*, is equivalent to an incompressible solid; but as the effectively liquid (*i. e.* irrotationally moving) portion of the medium cannot suffer any strain which calls up an opposing stress, it appears that in considering the strain-figure we should have to deal with the sponge-like compressible solid, made up of vortex-filaments.

9. *Gravitation*.—Disregarding this last speculation, let us return to the more general question of strain, and for simplicity take the case when the strain-figure is symmetrical about a point O. So far as this one strain-figure is concerned, we may, roughly speaking, divide the medium into two portions, in one of which the strain tends to increase, while in the other it tends to decrease. If these portions are separated by a single surface, then, in the present case of symmetry, this surface (A) will be spherical. On one side of A the medium will be so strained that a small additional strain of the same type would correspond to increased potential energy, while on the other side of A a small increase of strain would correspond to decreased potential energy. If the strain *outside* A corresponds to *increased* potential energy, two distant strain-figures will *repel* one another; but if the strain *outside* A corresponds to *decreased* potential energy, two distant strain-figures will *attract* one another. If gravitation is to be explained in accordance with the theory of this paper, the above would seem to indicate the nature of the explanation. There must be some type of strain which would of itself be produced in the medium, were it not that in some other portion of the medium there would be an accompanying strain of a type corresponding to stability. Perhaps we may also vaguely infer why the gravitative attraction exerted by a body is proportional to its mass, for we have supposed both

Fig. 2.



\* B. A. Report, 1887, p. 486; Phil. Mag., October 1887, p. 342.

† 'Nature,' May 9, 1889.

these quantities to be determined by the distribution of strain in the medium; it seems possible, indeed, that the greater part of the effective mass of a strain-figure might reside in that region where attraction follows the Newtonian law.

10. *Collision*.—If we bring the centres of two strain-figures close together, so that the spheres A intersect sufficiently far, we shall be partly superposing two strain-distributions of such a type that the energy increases with the strain, so that repulsion may, perhaps, ensue. Of course this is only a very rough attempt at explaining the effects of collision, and takes no account of any *deformation* which might be produced in the strain-figures on bringing their centres to such close quarters. But even were such deformation produced, the results of a collision might still be of a very simple character. So long as the condition of § 4 is satisfied, *so long, that is, as the motions concerned are extremely slow compared with V (the velocity with which gravitation is propagated) the distribution of displacement in the medium will be at each instant the same as if the two strain-figures were at rest.* Hence, though the two strain-figures may recoil from one another with altered velocities they will not have acquired any vibratory motion from the impact. This statement is equally true whether the strain-figure is symmetrical or not, but in the case of symmetry about a point, the properties of a strain-figure will be identical with those of a Boscovich particle, exerting actions at a distance according to a law of force.

11. The result just established has a bearing on the dynamical theory of heat. We know that the number of degrees of freedom of a molecule, and consequently also of an atom, is probably finite. If an atom consisted of  $n$  strain-figures of the most general kind, the total number of degrees of freedom would be  $6n$ ; but if each of the constituent strain-figures were symmetrical about a point the number would be reduced to  $3n$ . Since the spectra of elementary vapours teach us that the number of degrees of freedom, though finite, is usually very large, we are led to infer that most atoms are formed by the aggregation of a large number of strain-figures.

12. *Discrete Nature of Atoms*.—Why do the atoms form a discrete series, and why are all atoms of a given element identical in physical and chemical properties? These are questions which it would be difficult to answer, though it does not seem quite so difficult to point out a direction in which we may possibly look for an explanation. If an atom consists of a number of points endowed with inertia and with the power of exerting actions at a distance, it is hard to see how any explanation can be given: nor is the

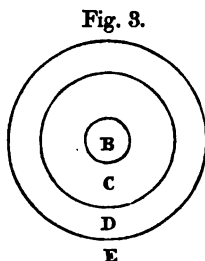


difficulty much less if the atom consists of a vortex ring or a vortex tangle, for we should then simply have to infer that the existing rings or tangles are as they are because they have always been so, and that an indefinite variety of rings or tangles of intermediate forms and sizes would be *à priori* perfectly possible. But if the atom consists of one or more strain-figures, the question becomes: Why do the strain-figures form a discrete series? Now we have conceived a strain-figure to be a disturbed condition of the medium, *which is of itself in stable equilibrium throughout*, and this immediately imposes an immense restriction on the possible varieties; since, also, the strains are impressed on a medium which would otherwise be homogeneous and isotropic, the conditions essential to stable equilibrium will be the same for all strain-figures, provided, that is, that the proximity of the centres of two or more does not disturb their form. But at this point a further assumption will be necessary; for if the turbulent motion or other structure of the medium were absolutely homogeneous (which implies infinite fine-grainedness), and if a strain-figure defined by a distribution of displacement  $A$  were a possible one, then the figure defined by the distribution  $A$  magnified  $n$  diameters would be equally possible. Thus the possible strain-figures, though infinitely restricted in variety by the conditions of equilibrium, would form not a discrete but a continuous series, or possibly a discrete system of continuous series. We must suppose, then, that the *coarse-grainedness* of the medium has an influence in determining the *size* of possible strain-figures.

13. *Physical Illustration.*—A very imperfect illustration of this last point may be drawn from a physical phenomenon; for consider a region free from the action of gravity and filled with a saturated vapour, which by some means is maintained at constant temperature and pressure. If compression takes place, liquid will be formed, and will exist in equilibrium with the vapour, no intermediate condition of the substance being consistent with equilibrium and stability. But, neglecting surface-tension, the liquid need not be formed in masses of any special size; that is, the possible sizes of the drops of liquid will form a continuous series. If, however, surface-tension is taken into account, the case is different; for suppose that the vapour is *slightly supersaturated*, and contains a number of spherical drops of liquid. Very large drops will continue to increase, and very small drops will diminish, while drops of one particular size (if any such are present) will just be in equilibrium with the vapour, although the equilibrium is necessarily unstable. But notwithstanding

that the analogy fails in this and in many other respects, it may serve to roughly illustrate the suggestion that the size of strain-figures, and consequently of atoms, is determined by the coarse-grainedness of the medium.

14. *Formation of Atoms.*—As regards the different varieties of atoms, we may conceive them to be made up of one kind or of several kinds of strain-figures. In place of the simpler form of fig. 2 we might for example imagine a form like fig. 3, where in the regions C, E the strain is such that the potential energy would decrease with increase of strain, while in the regions B, D the strain and the potential energy would increase together. We might also imagine distributions which were not spherical, in which case it might happen (§ 4) that the laws of motion were less simple than those of Newton. It would not then necessarily follow that an atom consisting of more than one strain-figure would possess the same complex dynamical properties, though I am not aware of any evidence that the separate atoms or molecules of a substance move in accordance with Newton's laws.



Of course the operation described in § 2 is not intended to represent the *formation* of a strain-figure, but merely to show that the *existence* of such a distribution is conceivably possible. If the ultimate fluid had long ago possessed motion of the most general kind, we might imagine its present condition to be due to the degeneration of that motion into a fine-grained turbulence; and if, in the quasi-solid so constituted, the existence of strain-figures were possible, it seems not unlikely that such would incidentally have been formed, unless the motion fulfilled special conditions. I would suggest then, very tentatively, *that if the distribution of motion in the ultimate fluid had fulfilled certain special conditions, there would have been no atomic matter in the universe, and that the existence of matter as we know it is an indication that such conditions were wanting.*

Concerning the possibility of the "transmutation" of elements, this investigation leads to no immediate conclusion, but any conceivable superposition of two strain-figures would probably involve only finite potential energy, so that the effect of a very severe direct encounter might be to make the two strain-figures pass *through* one another. It seems possible, too, that at some stage of the impact the distribution might resolve itself into one or more strain-figures of a different kind, the entire effective mass not being *necessarily* the same as before.

15. It may be remarked that, according to the assumptions of this paper, every motion in the universe is ultimately due to *stationary motion* in a quasi-solid medium. This medium, which extends through all known space, is supposed to be (at least appreciably) perfect in its elastic properties, that is, free from viscous yielding and internal friction; and its ever changing distribution of stress and strain is to be held accountable for all observed phenomena.

16. The subject of this paper being now explained, so far as the vagueness of my own views will allow, the fundamental proposition may be stated as follows:—

*A given portion of matter consists, not of any individual portion of æthereal or other substance, but of modifications in the structure or energy or other qualities of the æther, and when matter moves it is merely these modifications of structure or of energy or of other qualities which are transferred from one portion of the æther to another.*

The strain-figure has here been almost exclusively considered, and we have seen

(i) That provided the motion is slow compared with a certain velocity  $V$  (§ 4), a strain-figure will encounter no resistance in travelling through the æther, and will obey laws of motion which include Newton's Laws as a particular case.

(ii) That gravitative and inter-atomic forces may possibly be supposed to arise from the stresses which accompany the distribution of strain.

(iii) That a collision between two single strain-figures would not set them vibrating, so that an atom consisting of strain-figures would have a finite number of degrees of freedom, as required by the dynamical theory of heat.

(iv) That the size and nature of possible strain-figures, and therefore also of possible atoms, would be limited by the conditions of equilibrium, thus giving rise, perhaps, to a discrete series.

On the other hand, it is a special difficulty of my theory that we require some assumption as to the superposition of strain-figures to account for the fact that the mass of a material body is equal to the sum of the masses of its constituent particles.

In conclusion, I have to thank Mr. G. H. Bryan for his kindness in verifying some portions of the analysis, as well as for a suggestion which has immensely lessened the labour of calculation.

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*Note added November 21.*

In the discussion which followed this paper, Professor

Fitzgerald mentioned that in his lectures he had spoken of matter as possibly travelling through space in the same way that a drop of water travels through a block of ice. The idea involved is the same as that which forms the basis of the foregoing pages. I have availed myself of Professor Fitzgerald's criticism to amend some remarks contained in the earlier part of the paper, and there is just one thing more which I should like to add. Every opinion expressed in the paper is not to be taken as an essential part of the theory, and, indeed, the most I can hope from an investigation so obviously incomplete is that it may prove suggestive to those who are working at the subject.

XIX. *On the Density and Composition of Dilute Sulphuric Acid.*—No. II. By A. W. RÜCKER, M.A., F.R.S.\*

IN a paper on the "Densities of Sulphuric-Acid Solutions," which appeared in the January number of this Magazine, Mr. Pickering has replied to my criticism of one of his curves, which was published in September (Phil Mag. Sept. 1891, p. 304). I propose as briefly as possible to indicate the points in which he traverses my arguments, and the reasons why I do not think that his conclusions are justified.

(1) Mr. Pickering objects that my equation is "of a complex and highly artificial form." The question as to what is a "complex" expression may be more or less a matter of opinion. I can only say that I think Mr. Pickering will find that my equation lends itself to numerical computation much more easily than

$$y = a + bx + cx^2 + dx^3 + ex^4 + fx^5 + gx^6,$$

which he seems to consider comparatively simple.

He is also probably aware that every time he applies his bent ruler to the paper, he is employing a curve of which the equation involves elliptic integrals and is far more complex than that to which he objects.

Of course he might reply that the short portions of the elastic curve which he uses might be expressed with sufficient accuracy by simpler approximate formulæ. If this argument were valid, I might point out that he could get still simpler results and reduce all his curves to straight lines if he carried the process of subdivision further. It is in general the case that an equation which represents a long range of experiments will be more complex than one which applies to a few only. This affords no argument against its use as an

\* Communicated by the Author.

empirical expression of the facts unless the number of constants involved be inordinately large.

This brings me to the second of Mr. Pickering's arguments.

(2) The number of constants in my equation is so great that a close agreement with his results is not surprising.

I reply that it is not disputed that my curve covers a range greater than that embraced by three, and less than that embraced by five of his curves. If we assume that each one of these curves could be expressed with sufficient accuracy by means of approximate formulæ each of which involved two disposable constants only, it follows that Mr. Pickering expresses by the aid of 6 and 10 constants respectively ranges of which the first is somewhat less, and the second somewhat greater, than that which I cover by means of 7 constants. As the assumptions I have made are extremely favourable to Mr. Pickering, this shows that he cannot claim any superiority on this head.

(3) Mr. Pickering objects to the numbers given by those terms in my equation which occurred to me first being brought into harmony with experiment by means of another term.

What would he think if, when a computer had noticed that the results of certain experiments could be approximately expressed by means of the circle

$$x^2 + y^2 = r^2,$$

he was thereby debarred (though a better result could be thereby obtained) from converting the circle into the ellipse

$$x^2(1 - \alpha^2) + y^2 = r^2,$$

where  $\alpha$  is a small quantity. It is often only by first using a rough approximation that a formula for the results of experiment can be framed.

(4) Mr. Pickering regards the last term in my equation as a "hump," and the points at which it becomes and ceases to become important as "marking the practical starting of a fresh order of things."

This may be answered in the same way as the last argument.

The values of  $y$  given by the two equations  $y^2 = r^2 - x^2$  and  $y^2 = r^2 - x^2(1 - \alpha^2)$  agree when  $x = 0$ . Does Mr. Pickering think that if the results of observation are expressed more accurately by the latter, that the points in which the two corresponding values of  $y$  in the two curves become noticeably different mark "a practical starting of a fresh order of things" in the ellipse.

The projection of the ellipse beyond the circle is an integral

part of the representation of the experiments, not a "hump" upon a fundamental circle.

The only case in which Mr. Pickering's point of view is allowable is that in which the range expressed by the curve assumed to be fundamental is very much greater than that over which the assumed disturbance extends. In the case of my equation this is not so. If the last term be omitted, the curve fails to fit the experiments over more than half the range to which it applies, and fails entirely outside that range. The first terms have no sort of claim to be regarded as fundamental. All are alike empirical and must be taken together.

Further proofs of the weakness of such arguments are not wanting. If it is permissible thus to separate the terms of the equation, we may treat them in other ways.

The first part of my expression gives a straight line, which expresses Mr. Pickering's results very well (and with a slight modification would express them still better) between 46.94 per cent. and 58.94 per cent. Above the latter point a linear equation does not suffice. As this point is close to one of Mr. Pickering's breaks he might, by dividing my equation thus, have argued that it proved the existence of this break; but by separating the terms in another way he has been led to the opinion that this is the only break which the equation satisfactorily bridges.

A method of manipulating the symbols which leads to such discordant results is self-condemned. When Professor Lodge condemned in 'Nature' the use of empirical equations for detecting discontinuities, Mr. Pickering disclaimed the method. He is now using it in his defence. He makes different equations of my one by leaving out various terms at pleasure, and then proceeds to argue as though they had some physical meaning.

(5) Mr. Pickering contends that my curve extends to so small a distance beyond the first and last break alleged to exist within its range that it cannot be regarded as having bridged them.

Had I started close to one of Mr. Pickering's breaks, he would no doubt have argued that the fact that my curve did not apply beyond it proved the existence of a discontinuity. His conclusions would, however, have been disproved had I shown that his experimental results could be equally well represented by a series of discontinuous curves, each of which began within the range of a part of the curve which he considered continuous, and bridged continuously a part which he regarded as discontinuous. If these new curves had the same average length as his own, the distances of their extremities

from his breaks would have been equal to half the average length of his curves. This operation is in effect that which I have performed, except that I have fused into one the four curves which would have been necessary to cover the range considered; but the condition still holds, that an overlap at the extremities about equal to half the range of one of Mr. Pickering's curves is adequate.

Mr. Pickering finally finds seventeen breaks between 0 per cent. and 100 per cent.; *i. e.* he divides the curve into eighteen parts, the average range of which is 5.5 per cent. Half of this is 2.7 per cent., and the overlaps of my curve are 2.5 per cent. and 4 per cent. at the two ends respectively.

It is true that the distance between the breaks under consideration is considerably over the average for the whole range; but that no argument can be based on this is proved by the fact that in one case (*viz.* between 72.8 per cent. and 78 per cent.) it is a little less than the average.

As to Mr. Pickering's argument in the footnotes on p. 138, in which he urges the uncertainty of his own observations in support of the view that the end of my curve may be nearer to a break than appears from the numbers he himself quotes, I can only say, that a research cannot be propped up by its own uncertainty.

I have discussed these arguments of Mr. Pickering because I wish, as far as possible, to meet him on his own ground, but I must frankly say that I do not think the discussion can with advantage be carried further, and I hope that he will not think that I admit the validity of any further arguments he may adduce if I do not answer them.

No definite mathematical method for deciding how the results of a group of experiments can best be graphically or analytically represented exists.

Hence the discussion becomes a wearisome argument as to how a ruler may be held, whether curves have "humps" and the like.

I have answered Mr. Pickering's arguments on such points because I wished at the end to take a wider point of view without being charged with having evaded them.

The state of the question appears to me now to be as follows :—

Mr. Pickering claims to have established the existence of certain hydrates of sulphuric acid by detecting discontinuities in the curves which represent the physical properties of solutions of the acid. He asserts that the evidence is cumulative, but it would avowedly take months to examine it all in minute detail. I have therefore sampled it. I took what I have every reason to believe Mr. Pickering considers to be the best part of his work, the determination of the densities.

I chose that one of the four curves which appeared to me (judging from Mr. Pickering's figures) to be based on observations which were especially free from abnormal errors.

I chose that part of this curve which passed through the percentage corresponding to the hydrate which Mr. Pickering has isolated, and a range which is about one third of the whole. As the result there are now extant three representations of the part of the curve which I studied :—

(1) Mr. Pickering's drawings, which show four discontinuities.

(2) My curve, which Mr. Pickering frankly admits agrees with the "experimental results just as satisfactorily as [his] own drawings do" (p. 136).

(3) Mr. Pickering has himself put forward a new solution (footnote, p. 141) in which he divides the range into two parts by means of two curves, which agree with my single curve so closely that he himself states "that the magnitude of the error will not help us to decide between their respective merits."

Now amid all the discussion as to whether the results are best represented by continuous or discontinuous curves, one thing is certain. Any peculiarity in a curve on which argument is founded must be proved to be outside the error of experiment. No weight can be attached to a representation which is not unique in the sense that no other is compatible with the observations when all allowance is made for experimental error. Mr. Pickering's first solution (the four-break one) is not unique. He has himself offered another (one break) and I have contributed a third (no breaks), all of which by his own admission are such "that the magnitude of the error will not help us to decide between their respective merits."

Put briefly, the observations, accurate and numerous as they are, are not accurate enough and not numerous enough to decide whether the 18° density curve is or is not discontinuous between 47 per cent. and 80 per cent. This is what I claimed to have established, and Mr. Pickering has joined forces with me by producing a second solution of his own.

As to the deductions which are to be drawn from this conclusion, I have previously expressed the opinion that Mr. Pickering will enjoy a certain dialectical advantage until some of his other curves have been examined in detail, and that I do not intend to undertake that examination (which will be lengthy and troublesome) myself.

Absolutely convinced, as of course I am, of his *bona fides*, I am not disposed to ignore his arguments as to the concordance of his results, or to generalize hastily from my own



investigation. I do not therefore either affirm or deny his conclusions. I do affirm that they are supported by a rope of argument to the strength of which the one strand which I have tested contributes nothing. It is difficult to believe in discontinuities which their discoverer himself abandons in the heat of argument by showing that his original solution may be replaced by another in which three may be entire curves and parts of two others replaced by two only.

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XX. *On the Theory of Surface Forces.*—II. *Compressible Fluids.* By Lord RAYLEIGH, Sec. R.S.\*

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IN the first part of the paper published under the above title (Phil. Mag., Oct. and Dec. 1890) the theory of Young and Laplace was considered, and further developed in certain directions. The two leading assumptions of this theory are (1) that the range of the cohesive forces, though very small in comparison with the dimensions of ordinary bodies, is nevertheless large in comparison with molecular distances, so that matter may be treated as continuous; and (2) that the fluids considered are incompressible. So far as I am aware, there is at present no reason to suppose that the applicability of the results to actual matter is greatly prejudiced by imperfect fulfilment of (1); but, on the other hand, the assumption of incompressibility is a somewhat violent one, even in the cases of liquids, and altogether precludes the application of the theory to gases and vapours. In the present communication an attempt is made to extend the theory to compressible fluids, and especially to the case of a liquid in contact with its own vapour, retaining the first assumption of continuity, or rather of ultimate homogeneity. There will not be two opinions as to the advantage of the extension to compressible fluids; but some may perhaps be inclined to ask whether it is worth while to spend labour upon a theory which ignores the accumulated evidence before us in favour of molecular structure. To this the answer is that molecular theories are extremely difficult, and that the phenomenon of a change of state from vapour to liquid is of such extreme importance as to be worthy of all the light that can be thrown upon it. We shall see, I think, that a sufficient account can be given without introducing the consideration of molecules, which on this view belongs to another stage of the theory.

If  $p$  denote the ordinary hydrostatical pressure at any point in the interior of a self-attracting fluid,  $\rho$  the density, and  $V$  the potential, the equation of equilibrium is

\* Communicated by the Author.

$$dp = \rho dV. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If, as we shall here suppose, the matter be arranged in plane strata, the expression for the potential at any point is

$$V = 2\pi \int_{-\infty}^{+\infty} \rho' \psi(z) dz, \quad . \quad . \quad . \quad . \quad (2)$$

where  $\rho'$  is the density at a distance  $z$  from the point in question. Expanding in series, we may write

$$\rho' = \rho + z \frac{d\rho}{dz} + \frac{z^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} + \dots,$$

so that

$$V = 2K \cdot \rho + 2L \frac{d^2\rho}{dz^2} + \dots, \quad . \quad . \quad . \quad (3)$$

where

$$K = 2\pi \int_0^\infty \psi(z) dz, \quad L = \pi \int_0^\infty z^2 \psi(z) dz. \quad . \quad . \quad . \quad (4)$$

The integrals involving odd powers of  $z$  disappear in virtue of the relation  $\psi(-z) = \psi(z)$ .

We may use (3) to form an expression for the pressure applicable to regions of *uniform* density (and potential). Thus, integrating (1) from a place where  $\rho = \rho_1$  to one where  $\rho = \rho_2$ , we have

$$\begin{aligned} p_2 - p_1 &= \int \rho dV = [\rho V] - \int V d\rho \\ &= 2K(\rho_2^2 - \rho_1^2) - \int d\rho \{ 2K\rho + 2L \frac{d^2\rho}{dz^2} + \dots \} \\ &= K(\rho_2^2 - \rho_1^2) - \int d\rho \{ 2L \frac{d^2\rho}{dz^2} + \dots \}. \end{aligned}$$

In the latter integral each term vanishes. For example,

$$\int \frac{d^2\rho}{dz^2} d\rho = \frac{1}{2} \int d \left( \frac{d\rho}{dz} \right)^2 = \frac{1}{2} \left( \frac{d\rho}{dz} \right)^2 - \frac{1}{2} \left( \frac{d\rho}{dz} \right)^2,$$

and at the limits all the differential coefficients of  $\rho$  vanish by supposition. Thus, in the application to regions of uniform density—uniform, that is, through a space exceeding the range of the attractive forces,

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2); \quad . \quad . \quad . \quad . \quad (5)$$

or, as we may also write it,

$$p = \varpi + K\rho^2, \quad . \quad . \quad . \quad . \quad (6)$$

where  $\varpi$  is a constant, denoting what the value of  $p$  would be in a region where  $\rho = 0$ . We may regard  $\varpi$  as the *external* pressure operative upon the fluid. Equation (5) may also be

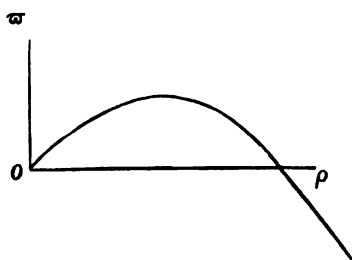
obtained, less analytically, by the argument employed upon a former occasion\*, and still more simply perhaps by consideration of the forces operative upon the entire mass of fluid included between the two strata in question regarded as a rigid body. It is very important to remember that *it ceases to apply at places where  $\rho$  is varying*, and that unless the strata are plane it requires correction even in its application to regions of uniform density.

In the case of a uniform medium, (6) gives the relation between the external pressure  $\omega$ , measured in experiments, and the total internal pressure  $p$ , found by adding to the former the intrinsic pressure  $K\rho^2$ . By the constitution of the medium, independently of the self-attracting property, there is a relation between  $p$  and  $\rho$ , and thence, by (6), between  $\omega$  and  $\rho$ . If we suppose that the medium, freed from self-attraction, would obey Boyle's law,  $p=k\rho$ , and

$$\omega = k\rho - K\rho^2. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

According to (7), when  $\rho$  is very small,  $\omega$  varies as  $\rho$ . As  $\rho$  increases,  $\omega$  increases with it, until  $\rho=k/2K$ , when  $\omega$  reaches a maximum. Beyond this point  $\omega$  diminishes as  $\rho$  increases, and this without limit. The curve which represents the relationship of  $\omega$  and  $\rho$  is a parabola; and it is evident that all beyond the vertex represents unstable conditions. For at any point on this portion the pressure diminishes as  $\rho$  increases. If, therefore, the original uniformity were slightly disturbed, without change of total volume, one part of the fluid becoming denser and the other rarer than before, the latter would tend still further to expand and the former to contract. And according to our equations the collapse would have no limit.

Fig. 1.



Points on the parabola between O and the vertex represent conditions which are stable so far as the interior of the fluid is concerned, but it may be necessary to consider the action of the walls upon the fluid situated in their neighbourhood. The simplest case is when the containing vessel, which may be a cylinder and piston, exercises no attraction upon the fluid. The fluid may then be compressed up to the vertex of

\* "On Laplace's Theory of Capillarity," Phil. Mag. Oct. 1883.

the parabola without losing its uniformity or becoming unstable. If, however, there be sufficient attraction between the walls of the vessel and the fluid, instability leading to total collapse will set in before the vertex is reached.

It will be seen that condensation to a denser state is easily explained, without any reference to molecules, as a direct consequence of self-attraction in a medium otherwise obeying Boyle's law. The objection that may be raised at this point is rather that the explanation is too good, inasmuch as it points to indefinite collapse, instead of to a high, but finite, contraction in the condensed part.

A simple and well-known modification provides an escape from a conclusion which follows inevitably from a rigorous application of Boyle's law. A provision is required to prevent extreme collapse, and this we may find in the assumption that a constant must be subtracted from the volume in order to obtain the quantity to which the pressure is proportional. In this case it is usual and convenient to express the relation by the volume  $v$  of the unit mass, rather than by the density. We have

$$p(v-b) = \text{constant},$$

$$\text{or} \quad (\varpi + K/v^2)(v-b) = \text{constant}, \quad . . . \quad (8)$$

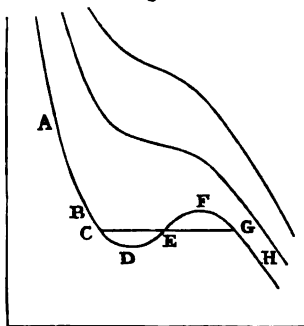
the well-known equation of Van der Waals. Here  $b$  is the smallest volume to which the fluid can be compressed; and under this law the collapse of the fluid is arrested at a certain stage, equilibrium being attained when the values of  $\varpi$  are again equal for the condensed and uncondensed parts of the fluid.

According to (8), there are three values of  $v$  corresponding to a given  $\varpi$ . Below the critical temperature the three values are real, and the isothermal curve assumes the form A B C D E F G H (fig. 2) suggested by Prof. James Thomson.

The part D F is unrealizable for a fluid in mass, being essentially unstable; but the parts A D, F H represent stable conditions, so far as the interior of the homogeneous fluid is concerned. The line C G represents the (external) pressure at which the vapour can exist in contact with the liquid in mass, and the isothermal found by experiment is usually said to be H G E C B A. This statement can hardly be defended.

If a vapour be compressed from H through G, it can only

Fig. 2.



travel along the straight line from G towards E under very peculiar conditions. Apart from the action of the walls of the containing vessel, and of suspended nuclei, the path from G to F must be followed. The path from G to E implies that the vapour at G is in contact with the liquid in mass. This is by supposition not the case; and the passage in question could only be the result of foreign matter whose properties happened to coincide with those of the liquid. If the walls attract the vapour less than the vapour attracts itself, they cannot promote condensation, and the path H G F must be pursued. In the contrary case condensation must begin before G is reached, although it may be to only a limited extent. Probably the latter is the state of things usually met with in practice. So soon as the walls are covered with a certain thickness of liquid, the path coincides with a portion of G E C, and the angle at G is only slightly rounded off.

Similar considerations apply at the other end of the straight course. If the liquid be expanded through C, it will not, in general, pass along C E, but will continue to pursue the curve C D, and will even attain the limit D, if the attraction of the walls upon the liquid be not less than that of the liquid upon itself. In the contrary case separation will suddenly occur at a point upon the wall, a bubble of vapour will be formed, and a point on the straight line C E will be attained. It is thus scarcely conceivable that a fluid should follow the broken course A B C E G H without some rounding of the corners, or else of overshooting the points C, G, with subsequent precipitation upon the line C E G.

A very important question is the position of the line C G. Maxwell\* showed that inasmuch as the area of the curve represents work performed at a constant temperature, it must be the same for the complete course as for the broken one. The line C G is therefore so situated as to cut off equal areas above and below.

This discussion is of course quite independent of the precise form of the relation between  $p$  and  $v$ . All that is necessary is such a modification of Boyle's law at great densities as will secure the fluid against indefinite collapse under the influence of its self-attraction.

We will now pass to the question of the transition from liquid to vapour, still supposing the strata to be plane. This is a problem considered by Maxwell in his article upon "Capillary Action" in the *Encyclopædia Britannica* †; but

\* 'Nature,' vol. xi. p. 358, 1875; Reprint, vol. ii. p. 418.

† Reprint, vol. ii. p. 560.

his solution appears to me to be vitiated by more than one oversight. By differentiation of (6) he obtains (with  $A$  written for  $K$ )

$$dp = 2A\rho d\rho,$$

and thence, by (1),

$$2A\rho d\rho = \rho dV;$$

so that

$$V = 2A\rho + \text{constant}.$$

In the subsequent argument the identity of  $A$  with  $K$  is overlooked; and the whole process is vitiated by the illegitimate differentiation of (6), which is only applicable at places where  $\rho$  is not varying. The final result, which appears to be arrived at without any assumption as to the physical connexion between  $p$  and  $\rho$ , is thus devoid of significance.

Let us integrate (1) from a place in the vapour round which the density has the uniform value  $\rho_1$  to a place in the liquid where the uniform density is  $\rho_2$ . Thus

$$\int_{(1)}^{(2)} \frac{dp}{\rho} = V_2 - V_1 = 2K(\rho_2 - \rho_1), \quad \dots \quad (9)$$

by (3). The external pressure is uniform throughout, and may be denoted by  $\varpi'$ ; and by (6),

$$\varpi' = p_1 - K\rho_1^2 = p_2 - K\rho_2^2. \quad \dots \quad (10)$$

At places where  $\rho$  is varying, that is in the transitional layer,  $\varpi$ , as given by (6), does not represent the external pressure; but we will still regard it as defined analytically by (6). Thus

$$\int_{(1)}^{(2)} \frac{dp}{\rho} = \int_{(1)}^{(2)} \frac{1}{\rho} \left( \frac{d\varpi}{d\rho} + 2K\rho \right) d\rho = \int_{(1)}^{(2)} \frac{1}{\rho} \frac{d\varpi}{d\rho} d\rho + 2K(\rho_2 - \rho_1), \dots \quad (11)$$

By comparison of (9) and (11),

$$\int_{(1)}^{(2)} \frac{1}{\rho} \frac{d\varpi}{d\rho} d\rho = 0; \quad \dots \quad (12)$$

or on integration by parts,

$$\left[ \frac{\varpi}{\rho} \right]_{(1)}^{(2)} + \int_{(1)}^{(2)} \frac{\varpi}{\rho^2} d\rho = 0.$$

The values of  $\varpi$  at the limits are the same, and have been denoted by  $\varpi'$ . Hence

$$\int_{(1)}^{(2)} \frac{\varpi - \varpi'}{\rho^2} d\rho = 0. \quad \dots \quad (13)$$

Since  $dp/\rho^2 \propto dv$ , this equation, obtained by purely hydrostatical methods applied to the liquid and vapour and the layer of transition between them, has precisely the same significance as Maxwell's theorem upon the position of the line C G in J. Thomson's diagram. In that theorem  $\varpi$  represents the external pressure that would be exerted by the fluid in various states of uniform density, some of which are not realizable. In the subject of the present investigation all the densities intermediate between those of the vapour and liquid actually occur; but, except at the extremities,  $\varpi$  no longer represents external pressure.

The explanation of the stable existence in the transitional layer of certain densities which would be unstable in mass, depends of course upon the fact that in the transitional layer the complete self-attraction due to the density is not developed in consequence of the rapid variation of density in the neighbourhood.

The distribution of density in the transitional layer, and the tension of the surface, can only be calculated upon the basis of a knowledge of the physical constitution of the fluid as expressed by the relation between  $p$  and  $\rho$ , and by the law of self-attraction. Poisson's contention that the surface-tension cannot be found upon the supposition of an abrupt transition from the liquid to its vapour is evidently justified; and since the thickness of the layer of transition is necessarily of the order of the range of the attraction, it follows that the correction for gradual transition is not likely to be small. A complete calculation of a particular case would be of interest, even on rather forced suppositions; but the mathematical difficulties are considerable. An approximate investigation might be conducted as follows:—

From (1) and (3),

$$\int \frac{dp}{\rho} = V = \rho \cdot 2K + \frac{d^2\rho}{dz^2} 2L + \dots$$

If we neglect the terms in  $d^4\rho/dz^4$ , &c., this becomes

$$2L \frac{d^2\rho}{dz^2} = \int \frac{dp}{\rho} - 2K \cdot \rho = f(\rho) - 2K \cdot \rho, \quad \dots \quad (14)$$

where  $f(\rho) = \int dp/\rho$  is a function of  $\rho$  given by the constitution of the medium.

Equation (14) may now be integrated by quadratures.

$$L \left( \frac{d\rho}{dz} \right)^2 = \int f(\rho) d\rho - K\rho^2,$$

and

$$z = L^{\frac{1}{2}} \int \left\{ \int \mathcal{A}(\rho) d\rho - K\rho^2 \right\}^{-\frac{1}{2}} d\rho. \quad (15)$$

It is possible that a graphical process would be found suitable. Equation (14) determines the curvature at any point of the curve representing the relation between  $\rho$  and  $z$  in terms of the coordinates and the slope.

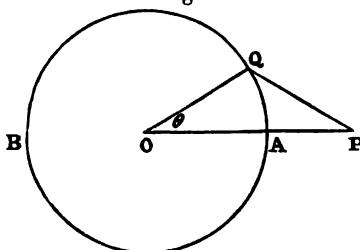
When the relation between  $\rho$  and  $z$  is known, the calculation of the surface-tension is a matter of quadratures. Probably the simplest way of considering the question is to regard the free surface as spherical (liquid within and vapour without), and to calculate the difference of pressures.

We have from (1),

$$p_2 - p_1 = [\rho V] - \int_{(1)}^{(2)} V d\rho = 2K(\rho_2^2 - \rho_1^2) - \int_{(1)}^{(2)} V \frac{d\rho}{dz} dz, \quad (16)$$

$z$  being measured outwards along the radius. The question is thus reduced to the determination of  $V$  at the various points

Fig. 3.



of the layer of transition, for all of which  $z = R$  approximately. Let P (fig. 3) be a point at which  $V$  is to be estimated, so that  $OP = z$ , and let AQB be a spherical shell of radius  $z - \zeta$ , of thickness  $d\zeta$ , and of density  $\rho'$ . We have first to estimate the potential  $dV$  of this shell at P.

The element of mass at Q is

$$\rho' \cdot 2\pi \sin \theta d\theta (z - \zeta)^2 d\zeta.$$

If, as before,  $\phi(f)$  express the ultimate law of attraction, and

$$\Pi(f) = \int_f^{\infty} \phi(f) df,$$

we have to multiply the above element of mass by  $\Pi(f)$ . Now

$$f^2 = PQ^2 = z^2 + (z - \zeta)^2 - 2z(z - \zeta) \cos \theta,$$

so that

$$-d \cos \theta = \frac{f df}{z(z - \zeta)}.$$



The element of the potential is therefore

$$\frac{2\pi\rho'(z-\zeta)d\zeta}{z} \cdot \Pi(f)f df.$$

In the integration the limits of  $f$  are AP and BP. The former is denoted by  $\zeta$ , and the latter may be identified with  $\infty$ , since  $z$  or  $R$  is supposed to be a very large multiple of the range of the forces. Accordingly for the potential at P of the whole shell, we have

$$dV = \frac{2\pi\rho'(z-\zeta)d\zeta\psi(\zeta)}{z}, \quad \dots \quad (17)$$

where, as usual,

$$\psi(\zeta) = \int_{\zeta}^{\infty} \Pi(f)f df. \quad \dots \quad (18)$$

To find the whole potential at P, (17) must be integrated with respect to  $\zeta$  from  $-\infty$  to  $+\infty$ ,  $\rho'$  being treated as a function of  $\zeta$ . As we need only consider P near the layer of transition,  $z$  in (17) may be identified with  $R$ .

If the transition is continuous, we may expand  $\rho'$  in the series

$$\rho' = \rho - \zeta \frac{d\rho}{dz} + \frac{\zeta^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} - \dots;$$

and then at the point P,

$$\begin{aligned} V &= 2\pi \int_{-\infty}^{+\infty} \left( \rho + \frac{\zeta^2}{1 \cdot 2} \frac{d^2\rho}{dz^2} + \dots \right) \zeta \psi(\zeta) d\zeta \\ &\quad + \frac{2\pi}{R} \int_{-\infty}^{+\infty} \left( \zeta \frac{d\rho}{dz} + \frac{\zeta^3}{1 \cdot 2 \cdot 3} \frac{d^3\rho}{dz^3} + \dots \right) \zeta \psi(\zeta) d\zeta \\ &= 2K \cdot \rho + 2L \frac{d^2\rho}{dz^2} + 2M \frac{d^4\rho}{dz^4} + 2N \frac{d^6\rho}{dz^6} + \dots \\ &\quad + \frac{2}{R} \left\{ 2L \frac{d\rho}{dz} + 4M \frac{d^3\rho}{dz^3} + 6N \frac{d^5\rho}{dz^5} + \dots \right\}, \quad \dots \quad (19) \end{aligned}$$

where (as in Maxwell's "Capillary Action")

$$\begin{aligned} K &= \pi \int_{-\infty}^{+\infty} \psi(\zeta) d\zeta, & L &= \frac{1}{2}\pi \int_{-\infty}^{+\infty} \zeta^2 \psi(\zeta) d\zeta, \\ M &= \frac{\pi}{4!} \int_{-\infty}^{+\infty} \zeta^4 \psi(\zeta) d\zeta, & N &= \frac{\pi}{6!} \int_{-\infty}^{+\infty} \zeta^6 \psi(\zeta) d\zeta. \quad \dots \quad (20) \end{aligned}$$

When (19) is multiplied by  $d\rho/dz$  and integrated across the whole layer of transition, we get for the part independent of  $R$ ,

$$2K \int_{(1)}^{(2)} \rho \frac{d\rho}{dz} dz = K(\rho_2^2 - \rho_1^2)$$

simply, all the other terms in  $L, M, \dots$  vanishing. Hence by (16), with integration by parts,

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2)$$

$$- \frac{2}{R} \left\{ 2L \int_{(1)}^{(2)} \left( \frac{d\rho}{dz} \right)^2 dz - 4M \int_{(1)}^{(2)} \left( \frac{d^2\rho}{dz^2} \right)^2 dz + 6N \int_{(1)}^{(2)} \left( \frac{d^3\rho}{dz^3} \right)^2 dz - \dots \right\} \dots (21)$$

The first term upon the right in (21) is the same as when the strata are plane. The second gives the capillary tension (T), and we conclude that when the transition is continuous

$$T = 2L \int_{(2)}^{(1)} \left( \frac{d\rho}{dz} \right)^2 dz - 4M \int_{(2)}^{(1)} \left( \frac{d^2\rho}{dz^2} \right)^2 dz + \dots \dots (22)$$

From these results we see that "the existence of a capillary force is connected with suddenness of transition from one medium to another, and that it may disappear altogether when the transition is sufficiently gradual"\*.

The series (22) would probably suffice for the calculation of surface-tension between liquid and vapour when once the law connecting  $\rho$  and  $z$  is known. It is possible, however, that its convergence would be inadequate, and in this respect it must certainly fail to give the result for an abrupt transition. In the latter case, where the whole variation of density occurs at one place, (16) becomes

$$p_2 - p_1 = 2K(\rho_2^2 - \rho_1^2) - (\rho_2 - \rho_1)V, \dots \dots (23)$$

$V$  relating to the place in question. And by (17)

$$V = \int_{-\infty}^{+\infty} 2\pi\rho'(1 - \xi/R)\psi(\xi)d\xi \\ = 2\pi(\rho_2 + \rho_1) \int_0^\infty \psi(\xi)d\xi - \frac{2\pi}{R}(\rho_2 - \rho_1) \int_0^\infty \xi\psi(\xi)d\xi.$$

Thus

$$p_2 - p_1 = K(\rho_2^2 - \rho_1^2) + 2T/R, \dots \dots (24)$$

\* "On Laplace's Theory of Capillarity," Phil. Mag. October 1883.

if

$$T = \pi \int_0^\infty \zeta_1 \psi(\zeta) d\zeta \cdot (\rho_2 - \rho_1)^2, \quad \dots \quad (25)$$

where (25) agrees with the value of the tension found for this case by Laplace.

In the application to a sphere of liquid surrounded by an atmosphere of vapour, equations (9), (11), (12) remain unchanged, in spite of the curvature of the surface. If  $\varpi''$  denote the external pressure acting upon the vapour,

$$p_1 = \varpi'' + K\rho_1^2, \quad \dots \quad (26)$$

$$p_2 = \varpi'' + K\rho_2^2 + 2T/R. \quad \dots \quad (27)$$

The symbol  $\varpi$  is still regarded as defined algebraically by (6), so that

$$\varpi_1 = \varpi'', \quad \varpi_2 = \varpi'' + 2T/R. \quad \dots \quad (28)$$

Integrating (12) by parts, we find

$$\frac{\varpi_2}{\rho_2} - \frac{\varpi_1}{\rho_1} + \int_{(1)}^{(2)} \frac{\varpi}{\rho^2} d\rho = 0;$$

or by (28),

$$\int_{(1)}^{(2)} \frac{\varpi - \varpi''}{\rho^2} d\rho + \frac{2T}{R\rho^2} = 0. \quad \dots \quad (29)$$

In this equation  $\varpi$  is a known function of  $\rho$ . If we compare it with (13), where  $\varpi'$  represents the external pressure of the vapour in contact with a *plane* surface of liquid, we shall be able to estimate the effect of the curvature. It is to be observed that the limits of integration are not the same in the two cases. If we retain  $\rho_1, \rho_2$  for the plane surface, and for the curved surface write  $\rho_1 + \delta\rho_1, \rho_2 + \delta\rho_2$ , we have from (29)

$$\frac{\varpi_2 - \varpi''}{\rho_2^2} \delta\rho_2 - \frac{\varpi_1 - \varpi''}{\rho_1^2} \delta\rho_1 + \int_{\rho_1}^{\rho_2} \frac{\varpi - \varpi''}{\rho^2} d\rho + \frac{2T}{R(\rho_2 + \delta\rho_2)} = 0;$$

or by (28),

$$\int_{\rho_1}^{\rho_2} \frac{\varpi - \varpi''}{\rho^2} d\rho + \frac{2T}{R\rho_2} = 0. \quad \dots \quad (30)$$

The limits of integration are now the same as in (13), so that by subtraction

$$(\varpi' - \varpi'') \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right) = \frac{2T}{R\rho_2},$$

or

$$\varpi'' = \varpi' + \frac{2T\rho_1}{\rho_2 - \rho_1}. \quad \dots \quad (31)$$

This is the value for the excess of vapour-pressure in equilibrium with a convex surface that is given in Maxwell's "Heat" as a deduction from Sir W. Thomson's principle.

The application of this principle may be extended in another direction. When liquid rises in a capillary tube open above, the more attenuated vapour at the upper level is in equilibrium with the concave surface, and the more dense vapour below is in equilibrium with the plane surface of the liquid. But, as was pointed out in the former paper, the rise of liquid is not limited to the height of the meniscus. Above that point the walls of the tube are coated with a layer of fluid, of gradually diminishing thickness, less than the range of forces, and extending to an immense height. *At every point the layer of fluid must be in equilibrium with the vapour to be found at the same level.* The data scarcely exist for anything like a precise estimate of the effect to be expected, but the argument suffices to show that a solid body brought into contact with vapour at a density which may be much below the so-called point of saturation will cover itself with a layer of fluid, and that this layer may be retained in some degree even in what passes for a good vacuum. The fluid composing the layer, though denser than the surrounding atmosphere of vapour, cannot properly be described as either liquid or gaseous.

In our atmosphere fresh surfaces, *e.g.* of split mica or of mercury, attract to themselves at once a coating of moisture. In a few hours this is replaced, or supplemented, by a layer of grease, which gives rise to a large variety of curious phenomena. In the case of mica the fresh surface conducts electricity, while an old surface, in which presumably the moisture has been replaced by grease, insulates well.

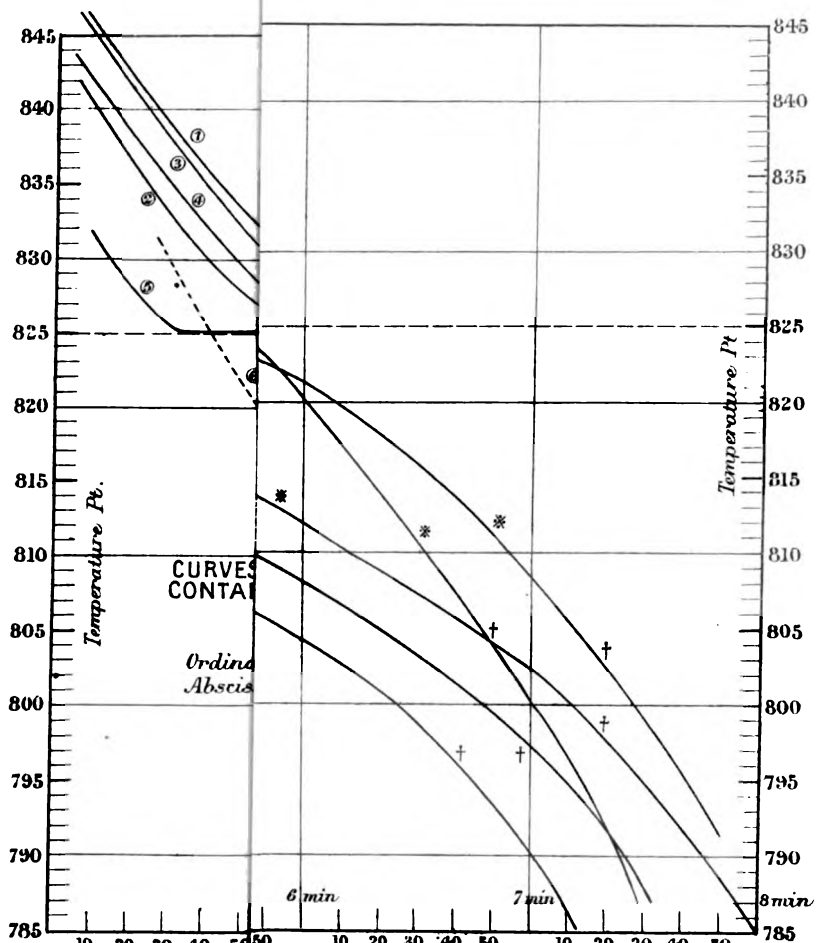
XXI. *Some Experiments with a Platinum Pyrometer on the Melting-points of Gold and Silver.* By H. L. CALLENDAR, M.A., Fellow of Trinity College, Cambridge\*.

[Plate V.]

IN a paper which appeared in the Philosophical Magazine for July 1891 I alluded to some experiments I had made with a platinum pyrometer on the melting-point of silver, and stated that the readings of these instruments were constant to a tenth of a degree at temperatures above 1000° C.

Through the kindness of Prof. Roberts-Austen I have recently had an opportunity of making some further experi-

\* Communicated by the Author.





ments on the melting-points of gold and silver at his laboratory at the Royal Mint. Professor Roberts-Austen himself suggested most of the experiments, and verified some of the observations. The results are interesting, not only as confirming his experiments, but also as showing the applicability of the platinum pyrometer to the accurate observation of small changes in the freezing-points of alloys at high temperatures.

The pyrometer used was constructed as described in my previous paper. It had a scale of 1 centimetre to the degree, and the galvanometer was so sensitive that it was possible to read the scale *with certainty* to a tenth of a degree at  $1000^{\circ}\text{C}$ .

The first experiment was an observation of the freezing-point of a specimen of gold containing as impurity a small percentage (0.05) of silver, which Prof. Roberts-Austen has shown to have very little effect in lowering the freezing-point, as it possesses very nearly the same atomic volume\*. It probably tends to crystallize out, when present in small quantities, isomorphously with the gold.

About 10 ounces of gold were melted in a clay crucible in a small Fletcher oxygen furnace and allowed to cool. The temperature of the metal was observed to fall rapidly till the freezing-point was reached. It then remained steady to a tenth of a degree for a minute or two at  $pt = 902^{\circ}.2$  (on the platinum scale) while the metal was solidifying. The gold was then again melted and well stirred and another reading was taken. The result found was  $pt = 902^{\circ}.3$ , differing by only a tenth of a degree from the preceding.

In order to test the effect of the addition of silver in lowering the freezing-point the mass was well heated, and 0.5 per cent. of silver was added to it. A rough observation taken while cooling gave  $pt = 901^{\circ}.5$ . The metal was again cautiously melted and continuously stirred while cooling. An observation of the freezing-point gave  $pt = 901^{\circ}.8$ . This was repeated with the result  $pt = 901^{\circ}.9$ . This seems to show that the effect of silver in lowering the freezing-point, though very slight, is still distinctly appreciable.

Some observations of the *melting-point* of the metal were taken as well as the freezing-point, but it was not found possible to make the conditions during heating as uniform as during cooling. It was observed that the temperature rose rapidly up to near the freezing-point and then very slowly for 2 or 3 degrees till the whole was melted, when the temperature again rose rapidly. The solid metal cannot be stirred, so that one part melts before the other, even if the

\* Proc. Roy. Soc., March 1891, p. 355.

heat be very gradually and uniformly applied ; but it was found that the more uniform and gradual the heating, the more closely the melting-point agreed with the freezing-point. In one case the whole of the metal was melted within half a degree above the freezing-point.

An experiment was then tried in order to ascertain the effect of adding aluminium to the gold contaminated with silver. The gold-silver alloy was raised to a temperature about  $10^{\circ}$  above its melting-point, and 0.5 per cent. of Al was added to it and stirred in with a red-hot pipe-clay rod. Considerable heat was evolved in the combination. As the mass cooled, portions of the metal began to solidify at the bottom at a temperature very little lower than the freezing-point of gold, but there was no well-defined arrest in the fall of temperature at any point. A layer of metal at the top remained in a gritty and pasty condition, as tested by the stirrer, and did not ultimately solidify till the mass had cooled down to a temperature of about  $600^{\circ}$  C.

The pyrometer was then melted out and tested for change of zero by comparing it with a mercury-thermometer in a vessel of cold water. No change of zero could be detected.

An experiment was next tried on the freezing-point of a nearly pure specimen of silver (99.97 per cent.). About 7 ounces of the metal were melted as before in the oxygen furnace. The temperature of the mass did not become quite steady during solidification, but fell slowly from  $pt=829.7$  to  $pt=829.0$ .

This result was somewhat unexpected. In my own experiments above mentioned I had used some 27 ounces of silver, the fineness of which was about 99.9 per cent. The freezing-point had always been sharply marked within a tenth of a degree of  $pt=830.0$  with this pyrometer. With the purer specimen now used we expected to find a higher result. On repeating the experiment, however, the same effect was observed. It was noticed that the silver began to "spit" violently about  $8^{\circ}$  below its freezing-point, and that its temperature fell some  $20^{\circ}$  very rapidly while the spitting continued\*. In my previous experiments the silver had been melted in a gas-furnace with an ordinary air-blast and a reducing-flame, and I had noticed very little spitting. Prof. Roberts-Austen suggested that the lowering of the freezing-

\* The fall of temperature was, at this stage, too rapid to allow accurate observations to be taken with the bridge-wire. Subsequent experiments by a different method show that "spitting" does not usually begin before  $814^{\circ}$  Pt., and that the fall of temperature is more rapid if there is no spitting.



point in the present case was probably due to the occlusion of oxygen.

The silver was therefore remelted cautiously with a smaller supply of oxygen, and care was taken not to heat it many degrees above its melting-point. The freezing-point was now much more sharply defined at  $pt = 829^{\circ}8$ , and there was far less spitting.

The experiment was again repeated, keeping a small supply of coal-gas on during cooling to prevent the absorption of oxygen. The freezing-point was now found to be quite clearly marked at  $pt = 830^{\circ}1$ .

The above observations show that the influence of the occluded oxygen cannot be neglected, and, further, that it has the effect, like many other impurities, of obliterating the sharpness of the freezing-point, as well as of lowering it. The experiments show, however, that it is possible to obtain very consistent results if precautions are taken to prevent the absorption of oxygen.

The silver was subsequently remelted and 0.5 per cent. of lead was added. The metal soon became covered with a film of molten oxide, although some gas was left on to retard the oxidation. The freezing-point of the alloy was fairly well defined at  $pt = 827^{\circ}8$ . On taking out the pyrometer it was noticed that the lead oxide had attacked the glaze on the porcelain tube. It was therefore again tested in cold water, but no change of zero could be detected.

The temperatures so far have all been expressed on the platinum scale. The reduction to the air-thermometer scale is still, unfortunately, subject to considerable uncertainty.

If we assume the empirical formula

$$t - pt = \delta \{ \overline{t/100} \}^2 - t/100 \}, \quad . . . . (d)$$

which holds very accurately at temperatures up to  $500^{\circ} \text{C.}$ , we find for the freezing-point of silver the value  $t = 981^{\circ}6 \text{C.}$  according to this pyrometer ( $\delta = 1.751$ ).

Becquerel and Riemsdyk, however, have both shown that the melting-point of silver is nearly the same as the boiling-point of zinc. The latter point has been determined by Deville and Troost\* with a porcelain air-thermometer with great care. They find the figure  $942^{\circ} \text{C.}$  as the mean of twenty-seven observations varying between  $954^{\circ}$  and  $929^{\circ}$ .

\* *Comptes Rendus*, xc. (1880), p. 773. Using hydrogen instead of air they found values between  $916^{\circ}$  and  $925^{\circ}$ ; using  $\text{CO}_2$ , values between  $1067^{\circ}$  and  $1079^{\circ}$ .

Le Chatelier has adopted for the graduation of his thermocouples the value  $945^{\circ}\text{C}$ .

I have myself made some direct experiments on the freezing-point of silver by means of air-thermometers with small bulbs, about 2 cubic centim. capacity, both of platinum and porcelain. These experiments point to a similar result, but cannot be considered very satisfactory. The platinum occludes gas, and the glaze of the porcelain cracks so that the material becomes porous. I hope shortly to be able to make some bulbs of fused silica, which is a far more refractory material, and ought to give better results.

If we take for the present the value  $945^{\circ}\text{C}$ ., and assume that the coefficient  $\delta$  in formula (d) is of the form  $(a+bt)$ , we find for this pyrometer  $a=2.050$ ,  $b=-.00065$ . Assuming these values, we find for the freezing-point of gold the figure  $t=1037^{\circ}\text{C}$ .

This is lower than the usually accepted figure  $1045^{\circ}\text{C}$ ., which rests mainly on the experiments of Violle; but if, as Roberts-Austen thinks probable\*, Violle's determinations of the specific heat of gold are low, the figure he (Violle) obtained for the melting-point of gold would be too high. The value  $t=1037^{\circ}\text{C}$ ., given above, may therefore prove to be the more correct.

The lowering of the freezing-point of the silver by the addition of 0.5 per cent. of lead was found to be  $2^{\circ}.3$  on the platinum scale. This becomes  $2^{\circ}.9$  when reduced to the air-thermometer scale.

The alloy was subsequently assayed at the Mint and proved to contain 0.54 per cent. of lead. This corresponds to 0.26 atoms of lead to 100 of silver. The fall produced per atom is therefore  $11^{\circ}.2$ . Assuming the latent heat of fusion of silver to be 21.07 (Person), the theoretical fall should be  $12^{\circ}.8$ . It appears that the composition of the alloy was not uniform, the upper portions being richer in lead. The agreement with the theoretical fall is therefore quite as close as could be expected. It may be noted that Heycock and Neville find that silver dissolved in lead lowers the freezing-point exactly to the extent predicted by theory on the assumption that its molecule is monatomic in solution.

I have since made some further experiments by a new method with a view to investigate more particularly the conditions under which silver absorbs oxygen, the extent to which its freezing-point is thereby lowered, and the temperature at which spitting occurs.

\* Proc. Roy. Soc. March 1891, p. 352.

To facilitate observations, the apparatus was so arranged that small changes of temperature could be followed and recorded by watching the movements of a spot of light reflected by the galvanometer-mirror on to a scale\*. The instrument was adjusted so that a deflexion of 40 millim. on the scale was equivalent to  $10^{\circ}$  Pt.

The silver was melted in the usual way and well stirred. The resistances in the box were adjusted approximately to the balance. Readings of the position of the spot of light on the scale were taken at intervals of 10 seconds as the mass cooled. These readings were plotted in the form of curves, as shown in Plate V., giving a continuous record of the cooling.

The uppermost of the curves, No. 1, is the record of the cooling of silver nearly free from oxygen. The temperature fell rapidly to  $830^{\circ}$ , the normal freezing-point. It then remained stationary to a tenth of a degree for about two minutes and a half. The lower part of the silver having by this time completely solidified while the upper part was still partially liquid, the temperature began to fall, slowly at first, and after about two minutes, when the whole mass was solid, very rapidly. A little spitting was noticed between  $810^{\circ}$  and  $805^{\circ}$  Pt., but it was extremely slight and faint.

The silver was then remelted and heated up to about  $890^{\circ}$  Pt. Oxygen was blown through it for about 30 or 40 seconds. This time the temperature fell to  $826^{\circ}$ , as shown in curve No. 2, before it began to freeze. The temperature remained nearly stationary at first, falling less than half a degree in the first minute. It then began to fall more rapidly. Spitting commenced at about  $814^{\circ}$ , and became very violent between  $810^{\circ}$  and  $805^{\circ}$ . It is evident from an inspection of the curve that much heat was *evolved* during the cooling, since the rate of cooling decreased considerably when the spitting was at a maximum. Shortly after the spitting ceased the temperature began to fall at the normal rate, as in curve No. 1.

The silver was then remelted with a reducing-flame, and another record of cooling was taken without the addition of oxygen. The curve proved to be an exact repetition of No. 1.

The silver was then heated to  $870^{\circ}$  Pt., and more oxygen passed for about a minute and a half. To my surprise, on cooling, it began to freeze at  $828^{\circ}8$ , as shown in curve 3,

\* For this purpose it was found necessary to compensate the galvanometer in such a way that its deflexions were independent of the temperature and resistance of its coils and of the strength of the battery.

and the spitting was much less violent. This seemed to show that silver would not absorb oxygen readily unless it was heated more than  $40^{\circ}$  Pt. above its melting-point. It was therefore again heated to  $890^{\circ}$ , and oxygen was passed for half a minute. The observations taken during cooling gave curve No. 4, which is almost a repetition of 2 except that less oxygen was absorbed. The silver was then heated up to  $910^{\circ}$  Pt., and oxygen was passed for two or three minutes with a view to saturate it. On cooling it began to freeze at  $825^{\circ}\cdot 1$ , as shown in curve 5. The spitting in this case was exceedingly violent. I have not succeeded in making the silver absorb a larger proportion of oxygen than this. A subsequent experiment, in which it was maintained at  $930^{\circ}$  while oxygen was passed for five minutes, gave a record which was almost an exact repetition of No. 4.

The greatest lowering of the freezing-point which I have observed in the case of silver saturated with oxygen in this way amounts to  $6^{\circ}\cdot 4$  C. This corresponds very nearly with a ratio of 1 molecule of oxygen to 200 molecules of silver. Assuming both molecules to have the same atomicity, we find that 100 grams of silver are capable of absorbing  $\cdot 074$  gram of oxygen, *i. e.* about  $5\frac{1}{2}$  times its volume of the gas. Gay-Lussac found that silver, when fused under nitrate of potash, absorbed in one case 22 times its volume of oxygen. Graham and Roberts-Austen have shown that spongy silver in the solid state at a red heat will absorb from 6 to 8 times its volume. It would have been interesting, had time permitted, to have made quantitative experiments, by some independent method, to determine the amount of oxygen absorbed in the present case.

A comparison of curves 1 and 4, in which the initial conditions and rates of cooling were the same, seems to indicate that the total heat evolved in the solidification of silver free from oxygen is *less* than in the case when oxygen is present. The quantity of heat evolved in the decomposition of the solution must therefore be considerable. The whole of the silver *appears* to be absolutely solid at a temperature at least  $10^{\circ}$  above the point at which it begins to spit. The heat evolved in spitting is sufficient to raise the extruded volcano of silver bubbles to a temperature considerably above its melting-point. A great deal of the heat is certainly dissipated in the volcano, where it cannot affect the pyrometer. The amount actually generated must therefore be considerably in excess of that indicated by the curves.

I have also made some further experiments by the same

method at the Mint, in conjunction with Professor Roberts-Austen, on the effect of gold dissolved in silver. We found that the addition of 0.6 per cent. of gold *raised* the freezing-point of silver by about  $0^{\circ}2$  C. A further addition of 0.6 per cent. raised the freezing-point  $0^{\circ}6$  C. in all. A further addition of 1.2 per cent., making 2.4 per cent. in all, raised the freezing-point  $1^{\circ}3$  C. It is interesting to observe that the effect of gold on silver is similar to that of silver on gold, and forms an exception to the general rule. It might have been expected, *à priori*, that the addition of 1.3 atoms of gold per 100 of silver would have *lowered* the freezing-point by about  $17^{\circ}$  C.; instead of which, a small but clearly marked *rise* was observed. Silver, as shown above, when dissolved in gold, produces a similarly slight but distinctly appreciable fall. It may be remarked that the rise produced by gold in silver bears nearly the same proportion to the interval between their freezing-points ( $945^{\circ}$  and  $1037^{\circ}$ ) as the number of atoms of gold present bears to the number of atoms of silver.

As a further experiment, aluminium was added to the mass in proportion (about 0.6 per cent.) sufficient to form, with the gold already in the silver, the alloy  $\text{AuAl}_2$ , which Roberts-Austen has shown to possess most interesting and remarkable properties. The mass was well stirred, and a curve of cooling was taken, shown by the dotted line (No. 6) in Plate V. The temperature fell to  $819^{\circ}$  Pt., where it remained quite stationary for about a minute. It then fell slowly for about two minutes, before the normal rate of cooling was reached. The lowering of the freezing-point  $12.3^{\circ}$  C. is rather less than that required by theory for a solution of 1.3 molecules of  $\text{AuAl}_2$  in 100 of silver; but it was observed that an appreciable quantity of the alloy sublimed about the mouth of the furnace and on the stem of the pyrometer. It is also doubtful whether the mass was perfectly homogeneous. The extent to which the freezing-point was lowered would, however, appear to indicate that this was a true case of solution.

From want of sufficient metallurgical knowledge, I cannot pretend to interpret these results more fully. I am induced to publish them, incomplete as they are, rather as an illustration of the degree of accuracy attainable by the use of platinum pyrometers, and in the hope that, in more experienced hands, they may lead to really valuable results.

I have also tested one of these pyrometers in molten cast iron raised to a temperature considerably above its melting-point. As the mass cooled it assumed a pasty condition, and

no well-defined freezing-point could be detected. The iron, however, was of very inferior quality, and by no means homogeneous. The glaze on the porcelain tube was attacked by the iron, but the pyrometer was otherwise uninjured and showed no change of zero. It should certainly be possible with these instruments to observe the effects of various impurities in altering the melting-point even of steel, and it is probable that the results in this case might be of some value to manufacturers.

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## XXII. *Notices respecting New Books.*

*Elementary Thermodynamics.* By J. PARKER, M.A.  
(Cambridge University Press.)

THIS is an interesting work. It bristles with originalities. They are not always quite sound, but originality seldom is. The book is very refreshing after the flood of text-books with which the world of students is inundated. It is not written to suit any syllabus. It is written to advance science by bringing forward the methods and views of the author. These methods and views, even where they are open to criticism from being ingeniously complex or unreally simple, are those of an ingenious and original mind, and are consequently worthy of serious consideration.

As the book is full of matter that it would be interesting to criticise, some few points only can be chosen. The division of forces into contact-forces and ether-forces is interesting, though the description of contact-forces which implies that particles are absolutely rigid is almost certainly an unreal simplification which is hardly required in order to justify Thermodynamic principles, and which, unless essential, should not have been introduced. This same unnecessary simplification leads to a very curious calculation as to the velocity of a molecule of ice (p. 118). Ether-forces are gravitation, radiation-forces (by which radiation moves particles), the causes of chemical, physical, electric, and magnetic actions. "Radiation-forces are, of course, far too small to be detected by instrumental means." Why "of course"? What about Tesla motors? To these radiation-forces he attributes comets' tails, without any the least explanation as to *how* they came to be due to the forces which move particles when a body is warmed by radiation. Though he divides the Energy of a system into Mechanical and non-Mechanical Energy, the latter being generally heat, he does not seem at first clearly to distinguish Matter Kinetic Energy and Ether Kinetic Energy. In these divisions and distinctions it would make it much easier to follow if the author had

condescended to give some examples illustrating his general statements. He revels in abstract generalities. It is very hard on the poor reader to dose him with these undiluted generalities, a little dilution with concrete cases would have made the dose much more palatable. His devotion to generalities is so great that he skips along in such a hurry when concrete questions arise that one can hardly see the sequence of his remarks. Take, for example, his description of Friction, § 14, and what seems to be intended for an explanation of its existence, but which neglects to explain how it is an irreversible action, although described as a purely mechanical effect due to the roughness of the surfaces. "... if two bodies, A and B, be pressed together, their surfaces of contact will sink into one another, and if we attempt to move one body over the other we shall experience a resistance in addition to the external forces." This statement about a force in addition to the external forces is in itself quite unintelligible, but it evidently omits to explain why a body is not just as much helped forward by running down into the roughnesses as it is stopped by having to be pushed up again out of them. Again, liquids are not rough, and yet there is what comes to the same as friction between their parts, and any really serious investigation of these questions should go much deeper than Mr. Parker does, or else should at least warn the student that the matter was not at all fully gone into. The author evidently despises the concrete. How else can he write that the latent heat of ice is "79.25 calories or 3,292,052,964 ergs"? Or, again, "41,539,759.8 ergs or about 3 foot-pounds"? Such a degree of accuracy should include the specific heat of the ether present, which Mr. Parker somehow ignores.

Similarly, in proving the concrete fact that the internal energy of a gas is independent of its density he gives the experiment with two reservoirs, a very bad method, and does not there give any reference to the very much more satisfactory porous-plug method, though he himself gives this method further on. In this same porous-plug experiment he does not condescend to give any discussion of why the gas does not become warmed like other bodies by friction. It is not because he is averse to investigating things to the bottom that he slurs over these things. He tries to get at general principles to explain everything. Take, for instance, his treatment of capillarity. He is not content to do this in the usual way. He is not content with the well-known method of calculating the thermodynamic relations thereof. No, he must found it directly on Carnot's theorem and the all-pervading friction. He assumes that the vessel, capillary tube, liquid, and all are carried sufficiently far down a mine or up a mountain for an observable change in the length of the column of liquid raised to be caused by the change in gravity. The tube must be given judicious taps, and at last we are to be satisfied that all is right because "it is obvious" that a certain expression must have a minimum value, when

it is not a bit more obvious than by the usual methods of investigation, which do not require such elaborate experimental foundations as this ingeniously complex method. In most of these applications of Carnot's principle, including such cases as the evolution of the planetary systems, of which he gives an interesting account, it does not seem quite clear whether friction is due to Carnot's principle or Carnot's principle due to friction, or whether they are the same. A general haziness as to this question lends a flavour of crankiness to much of the book. Much of it is, however, very interesting and most of it suggestive, as, for example, his consideration of the objection that animals are too efficient. He begins by the curious remark that they cannot be electromagnetic engines because "it is obvious that there is no sensible absorption of electric energy." Like others who border on crankdom, Mr. Parker is very fond of that "it is obvious." It is obvious, on the other hand, that there *seems* to be quite as much electric energy in bread and butter as in zinc, and zinc certainly can drive electromagnetic engines. But, as he points out, the real answer to any objection to Carnot's principle founded on the efficiency of animals is that animals are not examples of cyclic processes and that plants must be included to complete the cycle; and then, he might have remarked, the high temperature of the cycle is that at which the radiations that can act on plants are evolved in sufficient intensity to act on plants; and this is a temperature comparable with that of the sun.

Mr. Parker's method of investigating Carnot's theorem is interesting, partly because it is open to some objections. He starts from the axiom that no work can be done if heat be taken in and given out all at a single temperature. The axiom is unfortunately not true. If the working substance be reduced during part of its cycle to absolute zero, no heat need ever be given out. Notwithstanding this, there is considerable advantage in getting rid of "the coldest body available;" and if Mr. Parker had been content to give the investigation in a concrete form that could be "understood of the people," and not spread over several pages of generalities, his method might have had a chance of being read. As it is, most readers will be sickened by the first few pages. He tries to cover every possible case by the generality of his statements, and nevertheless makes all sorts of postulates that are passed over as evident, so that his argument, being horribly scholastic, hides most of the foundations on which it is based. He postulates in one place that giving heat by friction is so absolutely identical with giving heat by conduction, that the presence of a body is unnecessary from which heat is at one time absorbed by conduction when at another time heat is given to it by friction. Under such circumstances it is rather hard on this poor useful body to say that its presence is unnecessary without any further explanation.

The principal objection to Mr. Parker's presentation of Thermodynamic theory is that instead of calling attention continually to



the way in which Carnot's Theorem is dependent on our inability to deal individually with the irregular heat-energy of molecules, this view is kept quite in the background and the subject is based upon a set of scholastic generalities that throw very little light on the physical basis of Thermodynamics. Such presentations have in the past rather tended to obstruct than advance Science. And yet the book is suggestive and interesting. Even if it did no more than continually call to mind the ether as a *vera causa*, it would be worth studying; much more therefore does it deserve study, being, as it is, the work of an ingenious and original, if of a somewhat scholastic and cranky mind.

*Theory of Heat.* By J. CLERK MAXWELL, M.A., F.R.S. Tenth Edition, with corrections and additions by LORD RAYLEIGH, Sec. R.S. London: Longmans, 1891.

IF the name of Clerk Maxwell were not in itself a sufficient guarantee of the excellence of the book before us, the fact that it has already passed through nine editions and still remains the standard text-book on the theory of Heat, indicates very clearly the opinion of scientific students concerning it. But the advance of science does not permit of an unlimited number of stereotyped editions; consequently it now becomes necessary to revise, and make additions to, Maxwell's original treatise. There was no one who could accomplish this task more satisfactorily than Lord Rayleigh, and we are gratified to learn that he has found leisure enough to undertake it, and to add ten pages of matter relating mostly to capillary phenomena and the kinetic theory of gases and liquids.

The book may be divided into two parts, in one of which molar, and in the other molecular, phenomena are discussed. The first of these includes calorimetry, thermometry, and thermodynamics, and in it the idea of temperature is taken as a fundamental one. The second part treats of capillarity, diffusion, and the kinetic theory of gases, and it is there shown that temperature is measured by the mean kinetic energy of the molecules in the case of gases at any rate. The theory of the first part was as complete when Maxwell wrote his treatise as it is to-day, it being a logical sequence of the two propositions that energy is indestructible, and that heat always passes from a hotter to a colder body. Unless either of these axioms can be shown to be false the theory will receive but little addition or alteration, and it is not surprising that Lord Rayleigh should leave Maxwell's text unaltered, save for the addition of a little note concerning the liquefaction of the so-called permanent gases. There is one paragraph where a distinct advance might have been recorded, though it does not in the least affect any theory of heat. On p. 38 Maxwell speaks of the Fahrenheit scale of temperature as being "very generally used," and of the Centigrade scale as "coming into use." The

almost universal adoption of the latter scale in recent years seems to call for a short note to this passage.

The chapters on waves and radiation form a good connecting link between the molar and molecular phenomena. An error of the previous editions is repeated on p. 229 of the present one, where the quantity  $Q$  of the mathematical expression is stated to be the velocity of propagation of the wave, this latter being really equal to  $Qv$ .

In molecular physics many important advances have been made, and Lord Rayleigh has added some valuable notes on the theory of imperfect gases and of liquids, and on capillarity. Indeed, he may be said to have written a brief history of Laplace's capillary coefficient  $K$ , which represents the internal pressure in a gas or liquid resulting from the mutual attractions of its molecules, and which accounts for the observed cohesion of liquids. In evaporating a liquid this cohesion is overcome; and Dupré has shown that  $K$  is equal to the energy required to evaporate a cubic centimetre of the liquid (that is, the work-equivalent of the latent heat of unit volume). Van der Waals and Clausius assumed the existence of this pressure in order to account for the known deviations of gases from the laws of perfect gases, and they have succeeded in explaining these deviations, at any rate for gases and liquids near the critical point. The subject is exciting great interest at the present time, and many readers will be acquainted with the discussion in recent numbers of 'Nature' between Lord Rayleigh and Prof. Tait, concerning the proper application of Clausius's "equation of the virial" to the case of a gas or liquid with mutually attractive molecules of finite size. Lord Rayleigh, in his note on the virial and its applications, in the volume before us, steers quite clear of any controversial matter; indeed, we notice that he is as cautious as Maxwell was in treating as a mere assumption the view that the temperature of a liquid is measured by the mean kinetic energy of its molecules. In a recent paper Tait gives strong reasons to the contrary, derived from considering the equality of temperature in the various horizontal layers of a tall column of liquid under gravity. We venture to hope that when the eleventh edition of Maxwell's treatise appears, Lord Rayleigh will be in a position to give us more definite information on some of these knotty points, and that the advance in our knowledge will be such that he can add another ten pages of equally valuable matter.

JAMES L. HOWARD.

XXIII. *Intelligence and Miscellaneous Articles.*

## ON A CONSEQUENCE OF THE POISSON-MOSSOTTI THEORY.

BY GOTTLIEB ADLER.

POISSON'S theory of magnetic induction gives the magnetizing constant  $k$  as depending in a very simple manner on the ratio  $g$  of the space  $\epsilon$  actually occupied by the molecules of magnetic substance to the whole volume  $v$ .

For

$$k = \frac{3g}{4\pi(1-g)}, \text{ where } g = \frac{\epsilon}{v}. \quad (1)$$

The same equation holds also, as Mossotti has shown, for dielectric polarization, the magnitudes  $\epsilon$ ,  $v$ , and  $g$  having the same significance, except that  $k = (K-1)4\pi$ , where  $K$  is the dielectric constant of the substance.

As the ratio for iron was found to be  $g = 134/135$ , and therefore the space occupied by the molecules was so great as to be inconsistent with the idea of equal spherical molecules, Betti (*Lehrbuch der Potentialtheorie*, pp. 377, 378) was led to modify Poisson's fundamental assumption, and he thereby arrived at the expression

$$k = \frac{3g}{4\pi(1-3g)}, \quad (2)$$

which gave for iron  $g = 134/403$ ; thus the objection mentioned above, and first pointed out by Maxwell ('Electricity,' vol. ii. § 430; see also Mascart and Joubert's 'Electricity,' English translation, vol. i. p. 151), is removed.

In describing the phenomena of magnetic or dielectric polarization, since these are based on the magnitude  $k$  itself, it is quite immaterial whether we regard  $k$  as defined by the expressions (1) or by (2), or whether it is simply taken as an empirical constant. A decision is, however, in so far important, since formula (1) is taken by some authors as starting-point for a determination of the size of the molecules from the value  $g$ .

It is now perhaps remarkable, that when  $k$  is taken as defined by the formula (1), or by the function of  $g$  as defined by (2), at the same time we can deal with a second constant introduced by Helmholtz and Kirchhoff (Helmholtz, Wied. *Ann.* vol. xiii. p. 397, 1881; Kirchhoff, Wied. *Ann.* vol. xxiv. p. 55, 1885), and used for describing the pressures occurring in magnetic or dielectric polarized bodies :

$$k' = \frac{\partial k}{\partial \log v}.$$

For

$$k' = \frac{\partial k}{\partial \log v} = \frac{\partial k}{\partial g} \frac{\partial g}{\partial \log v} = -g \frac{\partial k}{\partial g},$$

as easily follows from (1).

Assuming Poisson's formula (1) we get

$$k' = \frac{\partial k}{\partial \log v} = -k \left( 1 + \frac{4\pi k}{3} \right). \quad (3)$$

*Phil. Mag.* S. 5. Vol. 33. No. 201. Feb. 1892. R

On the contrary, assuming Betti's formula (2),

$$k' = \frac{\partial k}{\partial \log x} = -k(1 + 4\pi k). \quad . . . . . (4)$$

Both formulas (3) and (4) give for the magnetizing number  $k$ , or for the dielectric constant  $K = 1 + 4\pi k$ , a decrease as the volume increases.

Both give for feebly magnetic or dielectrically polarizable substances, neglecting terms of higher order,

$$k' = \frac{\partial k}{\partial \log v} = -k, \quad . . . . . (5)$$

but otherwise  $k'$  as a quadratic function of  $k$ , and therefore agreeing in the order of magnitude.

From the experimental results on the dependence of  $k$  on the increase of volume a decision is possible, whether Poisson's or Betti's formula is in accordance with facts.

The only direct experimental results on this view are in the case of gases.

The measurements of Boltzmann show that the dielectric constant increases directly with the pressure. If with Boltzmann we make the further assumption that the proportionality of the increase of the dielectric constant with increase of pressure holds up to complete exhaustion, his results may be embraced within two formulas propounded by him, the first of which is the dielectric constant for the normal pressure of an atmosphere,

$$K_1 = 1 + \lambda, \quad . . . . . (6 a)$$

while the other fixes its dependence on the pressure  $p$  by

$$K = (1 + \lambda p). \quad . . . . . (6)$$

From (6) we have

$$\frac{\partial K}{\partial \log p} = \lambda p = K - 1 = 4\pi k.$$

Now for a gas  $pv = \text{const.}$ , and accordingly  $d \log p = -d \log v$ ; hence

$$-\frac{\partial K}{\log p} = \frac{\partial K}{\partial \log v} = 4\pi k' = -4\pi k,$$

from which we get the formula (5) deduced from Poisson's and Betti's formula,

$$k' = -k.$$

There are no direct experimental results as to the change of  $k$  with the volume except in the case of gases.

From the theory of Helmholtz and Kirchhoff as to the change of shape of magnetic or dielectric polarized bodies, the magnitude of  $k'$  together with  $k$  is decisive as to the change of volume

which these bodies experience in the electrical or in the magnetic field.

Experiments which Quincke \* made with liquids in the electrical field have shown that substances which have almost the same dielectric constant have a totally different behaviour as regards change of volume †. This seems to favour the supposition that at any rate in this case  $k'$  is an independent constant characteristic of individual substances. Hence for these substances Poisson's (1) or Betti's (2) formula, which appears to connect  $k'$  with  $k$  in a perfectly definite manner defined by formulas (3) and (4), seems to be in disaccord with experiment; for these substances  $k$  must be regarded simply as an empirical constant.

It follows further from these considerations that the application by many authors of Poisson's formula to the determination of the fraction  $g$  of the volume actually occupied by the molecules is only allowable in the case of gases, but for other substances is wanting in accuracy.—Wied. *Annalen*, vol. xlv. p. 173.

#### ON THE ELECTROMOTIVE FORCE OF GAS BATTERIES.

BY GERTSCHO MARKOVSKY.

The results of these experiments may be stated in the following terms:—

1. The electromotive force of a platinum plate coated with hydrogen against a platinum plate in sulphuric acid freed from gas, has not the value which has been previously assumed. For hydrogen the force is smaller, that is = 0.646 volt and for oxygen greater = 0.374 volt.

2. Hydrogen and oxygen gases developed electrolytically act just in the same way as when formed by purely chemical action.

3. By the addition of solution of platinum sulphate the electromotive force of an oxygen element is diminished, while that of a hydrogen one increases, and in such a manner that the electromotive force of an oxygen-hydrogen element is not changed by the addition of solution of platinum sulphate.

4. The electromotive force is independent of the change of density and temperature of the gas introduced.

5. Carbon electrodes behave in a gas element, or when polarized by a current, differently from platinum electrodes.—Wiedemann's *Annalen*, vol. xi., 1891.

\* Wied. *Ann.* vol. x. p. 523, 1880.

† Thus for oil of turpentine, where

$$K = 2.412, \quad \frac{\Delta v}{v \cdot 10^6} = 1.7;$$

for petroleum, where

$$K = 2.124, \quad \frac{\Delta v}{v \cdot 10^6} = 19.23;$$

for rape oil, where

$$K = 2.442, \quad \frac{\Delta v}{v} = -18.24 \cdot 10^{-6};$$

and therefore a decrease.

## VELOCITY OF SOUND IN MEMBRANOUS BODIES.

BY F. MELDE.

The author gives the following extract from a longer memoir which is shortly to appear.

By membranous bodies he understands such bodies as are capable of forming a membrane, which can be used for all purposes for which membranes can be applied. To these belong, for instance, the various kinds of paper, linen and cotton materials, caoutchouc, animal membranes, and so forth. The velocity of sound in such bodies differs greatly, but can be easily determined by fixing narrow strips at both ends, rubbing them in the middle, and determining the pitch of the fundamental note. If the number of vibrations is  $n$ , and the length of the strip  $L$ , then

$L = \frac{\lambda}{2}$  and  $2L = \lambda$  = the wave-length of the note in question; so

that the velocity is  $v = n\lambda$ . In this way the following numbers were obtained for the velocity of sound.

	Metres.
Paper soaked with wax. . . . .	3040
Stout red parchment-paper . . . . .	2960
Yellow silk paper . . . . .	2046
Drawing-paper . . . . .	1955
Smooth green paper . . . . .	1952
Yellow satin ribbon . . . . .	1950
Black paper . . . . .	1923
Red paper . . . . .	1852
Hemp string . . . . .	1720
Cotton string . . . . .	1280
Coloured cross-ribbed silk ribbon . . . . .	930
Black wax cloth . . . . .	570

*Beiblätter der Physik*, vol. xv. p. 756.

## THE SOLITARY WAVE : CORRECTION OF A SIGN.

*To the Editors of the Philosophical Magazine and Journal.*

University College, Dundee,  
January 12, 1892.

GENTLEMEN,

In my "Note supplementary to a Paper on the Solitary Wave," which appeared in the December number of your Magazine, one of the expressions is written with a wrong sign, and might therefore prove somewhat misleading. The series given in the second line of page 555, the expansion of equation (5) of my paper "On the Solitary Wave" (*Phil. Mag.* July 1891), for the case of  $x$  negative, should be affected with the negative sign. Were this not corrected it might appear to affect the argument, at least if one were to attend only to the series as written, neglecting its connexion with (5).

I am, Gentlemen,

Yours faithfully,

JOHN M'COWAN.

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# CONTENTS OF N° 201.—*Fifth Series.*

---

XVI. On the Generalizations of Van der Waals regarding "Corresponding" Temperatures, Pressures, and Volumes. By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol. (Plates I.—III.) ..... page 153

XVII. The Construction of Non-Inductive Resistances. By Prof. W. E. AYRTON, F.R.S., and T. MATHER. (Plate IV.) ..... 186

XVIII. A Theory concerning the Constitution of Matter. By CHARLES V. BURTON, D.Sc. .... 191

XIX. On the Density and Composition of Dilute Sulphuric Acid.—No. II. By A. W. RÜCKER, M.A., F.R.S. ... 204

XX. On the Theory of Surface Forces.—II. Compressible Fluids. By Lord RAYLEIGH, Sec. R.S. .... 209

XXI. Some Experiments with a Platinum Pyrometer on the Melting-points of Gold and Silver. By H. L. CALLENDAR, M.A., Fellow of Trinity College, Cambridge. (Plate V.) ..... 220

XXII. Notices respecting New Books :—MR. J. PARKER'S *Elementary Thermodynamics*; CLERK MAXWELL'S *Theory of Heat*, Tenth Edition edited by Lord Rayleigh ..... 228, 231

## XXIII. Intelligence and Miscellaneous Articles :—

- On a Consequence of the Poisson-Mossotti Theory, by Gottlieb Adler ..... 233
  - On the Electromotive Force of Gas-Batteries, by Gertscho Markovsky ..... 235
  - Velocity of Sound in Membranous Bodies, by F. Melde ..... 236
  - The Solitary Wave: Correction of a Sign ..... 236
- 

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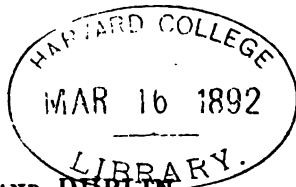
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THE  
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[FIFTH SERIES.]

MARCH 1892.

XXIV. *Petrological Notes on the Euphotide or Saussurite-smaragdite Gabbro of the Saasthal.* By Professor T. G. BONNEY, D.Sc., LL.D., F.R.S., &c.\*

EVERY geologist has heard of, many have seen, the erratics of this peculiar variety of euphotide, which are so abundant in the upper part of the Saasthal, and are more sparingly distributed over the southern portion of the Swiss lowland. But though they have been noticed by some foreign authors †, and are frequently mentioned by English ‡, the only attempt at a complete history of them in our language is to be found in a brief abstract of a paper by Captain Marshall Hall §. The author, however, was not very successful in obtaining good specimens and was unable to arrive at any very definite conclusions, so that some account of my own examination may be useful, at any rate to English students.

\* Communicated by the Author.

† E. g. at some length by R. Hagge, *Mikroskop. Untersuch. üb. Gabbro u. verw. Gesteine*. Referred to briefly by Rosenbusch, *Mikrosk. Physio-graphen*, s. v. Gabbro.

‡ "Contributions to the History of Euphotide and Saussurite" (T. Sterry Hunt, Amer. Journ. Sci. xxvii. p. 333, 1859) contains a number of historical references, and gives the result of a chemical and mineralogical investigation of this group of rocks. But as it is founded on a study of hand-specimens only, and these were not examined with the microscope, some of the conclusions appear to me to hold good only in a mineralogical, not in a petrological sense.

§ Mineralogical Magazine, vol. v. p. 194.

*Phil. Mag.* S. 5. Vol. 33. No. 202. March 1892.

S

These erratics\*, which abound between Saas and the end of the Allalein glacier, are derived from the extremity of a long curving spur, which runs eastward from the summit of the Allaleinhorn (13,235 feet) and divides the *névés* of the Allalein and Hochlaub glaciers. This is indicated on the Swiss map by the figures 3150 m. (=10,334·8 ft.). On the Geological Map (Blatt xxiii.) it is coloured "serpentine," but this term is used by the surveyors with singular elasticity. For instance, in the neighbourhood of the Saasthal it denotes not only true serpentine, of which there is a fair amount, but also gabbro, and a rather hard schistose rock, which contains green hornblende, chlorite, epidote, and probably felspar, often garnet, sometimes glaucophane, and so has no more claim than a diorite to be called a serpentine. The more obvious point of departure for this spur is the little inn at the Mattmark See, from which I think it might be reached in about three hours' walking; but it can be visited without much difficulty from Saas Fee. For guidance by this route and for much valuable aid in collecting these notes I am indebted to my friend Mr. Jas. Eccles, F.G.S., who had already made the expedition in 1890 †.

This ridge of gabbro is completely surrounded by snow and ice, beneath which, however, it is doubtless linked to the spur of the Allaleinhorn. Evidence of this may be found in two small knolls or heaps of boulders which protrude from the snow, one slightly on the Allalein side, the other on the Hoch-

\* They have been long known to me, and in 1881 I endeavoured to reach the ridge. Unfortunately I was obliged to turn back and have had to wait ten years for another opportunity.

† There are two routes from Saas Fee (5900 feet). The one passes up the right bank of the Fee glacier till it reaches a "col" (9872 feet) beneath the precipices of the Eggnerhorn. This leads on to the *névé* of the Kessjen glacier. Crossing this we make (roughly in a S.S.E. direction) for a gap in the bounding ridge, on the left of which is a mass of light-coloured calc-mica schist. Descending from this gap (probably about 10,095 feet) we can scramble down along the rocks in the direction of the Hinter Allaleinhorn until it becomes easier to take to the *névé* of the Hochlaub glacier, and we cross this to the gabbro ridge.—The other route turns to the right just before reaching the first col, ascends the snow slopes of the ridge from the Hinter Allaleinhorn obliquely so as to get above some ugly *seracs*; then, after crossing a bergschrund, mounts to the summit of the "grat." This is followed to near the base of the peak itself, when it becomes easy to descend to the *névé* of the Hochlaub glacier. We went by the former way and returned by the other; this is higher (being by aneroid—which that day gave good results—10,800 feet) but a little more direct. It presents no difficulties to persons familiar with Alpine excursions; on either route a rope is useful. We were about 4½ hours going and 3 hours returning, without hurrying.

laub side\* of the flattened snow-saddle between the two glacier basins. These knolls, as will presently be described, also consist of a variety of gabbro. The ridge of which we speak rises slightly from beneath the snow, and runs pretty nearly on a level for about a couple of hundred yards, falling steeply on either side towards the descending surface of the glaciers. At the end, which falls no less steeply, it may be 200 feet above the ice†. Mr. Eccles, in 1890, also found gabbro in the above-named spur of the Allaleinhorn, but the mass of it appeared to be small. I think these are all the visible outcrops of any importance. That they are limited to the vicinity of this peak is shown by the fact that we find the erratics cease in the Saasthal as soon as we have got beyond the right moraine of the Allalein glacier. We look for them in vain over the stone-strewn bed of the valley above the Mattmark See.

Before describing the rock of these ridges it will be convenient to make some remarks on that of the boulders, where really it is more conveniently examined, thousands of specimens being, as it were, laid out for our inspection. There are many varieties, some of which are much more numerous than others. I noticed the following :—

(1) A gabbro consisting mainly of felspar, varying from a rather glassy bluish-white to white (that is to say, a somewhat altered labradorite), and a brownish diallage, with lustre not conspicuously metallic. Structure often ophitic. Varieties occur from rather fine-grained to coarse, when the crystals may be an inch or so long. Not common.

(2) Specimens chiefly consisting of a greyish-white saussurite and a rather acicular hornblende of a dull slate-blue colour, sometimes also containing pale-red garnet. Rare.

(3) Specimens with but little of the pyroxenic constituent, consisting mainly of saussurite and a pale reddish granular mineral (garnet). Not very common.

(4) A rock consisting of a white, rather granular, feldspathic mineral, and a rather fibrous hornblende, deeper and duller in colour than the smaragdite and of a more actinolitic habit. The two minerals occur generally in irregularly shaped

\* The latter is so small that it is omitted (necessarily) on the Swiss map.

† These were our estimates at the time. The Swiss map, if it is intended to be strictly accurate, would add about 50 yards to the length. Captain Marshall Hall states that he was three quarters of an hour climbing up the end of the wall. Either he must have found exceptional difficulties or we have underestimated the height.

patches with a slight approach to foliation, though traces of an ophitic structure may sometimes be observed. The structure resembles, though it is less definite and on a coarser scale, that figured on plate xliii. in Mr. Teall's 'British Petrography' (a gabbro from the Lizard district). Common.

(5) The typical "euphotide," consisting of white or almost white saussurite, and bright green smaragdite, structure granular to ophitic, texture moderately coarse to very coarse (patches of either mineral up to full 2 inches in diameter). Very common.

It must not, however, be supposed that these different types can be separated by hard and fast lines. In the same block one variety may pass into another, such as (3) into (5), or even (4) into (5), by the gradual incoming of smaragdite, at first in a "spotty" fashion, and by induration of the felspathic constituent, or a coarse and a fine variety may be associated in a way to which we shall have again to refer.

How far, then, are these types represented in the ridge? We struck it on the northern side, near to the western end, where it rises from the snow, and went to the other one along its crest\*. On returning, we left the ridge by its southern face. The greater part, so far as we could see it, consists of the hornblendic variety of the gabbro (4), which, however, occasionally loses this schistose structure and becomes normally holocrystalline. Smaragdite occurs only locally. Occasionally also the rock becomes slightly streaked or banded by the incoming of lines of darker, more hornblendic, rock. We met with no evidence here which was conclusive as to the origin of the foliation. The ordinary structure might not unreasonably be claimed as a result of dynamo-metamorphism, but the last-named one seems to require some other explanation. We found a few thin dyke-like masses of a more compact rock, some of which reminded me of that generally fine-grained augitic or hornblendic rock which breaks into, but is intimately associated with, the gabbro at the Lizard. The smaragdite-euphotide occurs, so far as we saw, only at the eastern end of the ridge; more abundantly, it is my impression, on the southern than on the northern side†. We observed the normal type (5) and occasionally the one with little smaragdite (3); we also noticed that the

\* This consists rather of a pile of separate blocks than of solid rock. As is common in mountainous regions, the "coping stones" of the wall are more or less displaced.

† Captain Marshall Hall also found it on the crags at the eastern end, and I have no doubt that it occurs in other parts of the ridge, but in those which we saw it was certainly subordinate to the other variety.

coarser varieties of the former appeared either in streaks or in vein-like masses in the ordinary rock, without, however, any sharp line of demarcation. In fact (as I wrote in my notebook at the time) all the varieties of gabbro seen on the ridge "seem to change rapidly one into another without any marked divisional lines, just as the coarser and finer, or the more and the less felspathic masses of the Lizard gabbro pass one into another—that is, they are all variations of one mass," the distinctive characteristics being due to differences, probably slight, either of chemical composition or of environment. The small outcrop on the southern side of the snow-saddle consists mainly of the hornblendic variety (4), and that on the northern side wholly, so far as we saw. A specimen brought by Mr. Eccles from the exposure in the spur of the Allaleinhorn shows this to be the same rock.

So much has been already written upon the microscopic structures of gabbros, and the varieties of rock into which they pass, that a brief notice will suffice for most of those from the Saasthal. In the specimens which I have examined the "saussurite" (as is usually the case) appears to be a rather variable aggregate of minute minerals. Among these, two kinds can be often distinguished: one varying from fibrous to prismatic, fairly clear, giving, with crossed nicols, bright tints with a fibrous-speckled aspect; the other, rather more distinctly fibrous and occurring in patches of a dusty aspect, but feebly translucent, and apparently having weak double-refractive power, for the tints are duller. In one or two specimens, however, notably in the variety (4), the constituents are larger and better defined. Here zoisite may be recognized abundantly in prisms sometimes about .03 inch long, with a fairly marked pinacoidal cleavage, and an occasional basal one. It is very slightly fibrous in structure, and gives low polarization-tints with straight extinction. There is also some colourless epidote, a flake or two of white mica, and a little interstitial quartz. Here and there small patches of fibrous hornblende are interspersed. So this "saussurite" consists of more than one microlithic mineral, and is undoubtedly an alteration-product of a lime-felspar\*.

The smaragdite in the hand-specimens often shows distinct cleavage-planes, sometimes resembling those of a diallage, as if it occurred in large crystals; but we find these on micro-

\* "If, then, we combine the researches of Lossen, Kloos, and Cathrein, we seem justified in concluding that a basic felspar may be replaced by albite and epidote, zoisite, or a zeolite of the scolecite group." Teall, 'British Petrography,' p. 152 (*et ante*).

scopic examination to be really composed of an aggregate of minute crystalline grains, which, however, in certain cases, show signs of orientation. Now and then traces of an old cleavage with a diallage-habit may be detected ; in other cases these are distinct and extinction with them ranges up to about  $40^{\circ}$ , but the grains are interstreaked, pierced, or sometimes traversed by zones (as if filling cracks) of a nearly colourless mineral resembling actinolite, and extinguishing at angles less than  $20^{\circ}$ . In other cases the smaragdite occurs in grains, almost colourless in thin slices, which sometimes show the characteristic cleavage of hornblende, and give its extinction-angle, but occasionally the latter indicates that an augite (omphacite) is also present\*.

The green hornblende in (4) is often bordered by a pale fibrous actinolite, and sometimes by well crystallized pale-coloured hornblende ; but the greater part of the patch retains traces of a former close cleavage as above described, but now consists of a rather fibrous pale green hornblende, which, though composite in character, exhibits a rudely parallel orientation, the whole being much clouded by dusty lines and patches. High powers show many of them to consist of minute belonites, and here and there needles of rutile can be identified. This form is also found in some of the other varieties of the euphotide, *e. g.* together with the "slate-blue" hornblende of (2). Here it is rather "muddy" looking, containing minute enclosures and tiny brown films ; the microliths by their general orientation seem related to some occasional faint lines, which may be indications of a former cleavage : the films may be traces of "schillerization."

The "slate-blue" hornblende in (2) occurs in "nests" of irregular form, roughly resembling sections of amygdaloids in a scoriaceous rock. It is sometimes idiomorphic, sometimes rather fibrous in structure and irregular in shape. It varies from colourless to a very pale blue, and is not strongly dichroic, changing in longitudinal sections from almost colourless to a pale violet-blue, in transverse sections from bluish to a faint purple. Evidently it is one of the paler varieties of glaucophane†. The mineral usually is fairly free

\* I have seen the mineral with characteristic augite cleavage in some smaragdite rocks, but do not find a thoroughly satisfactory specimen in any of my slides from the Saasthal.

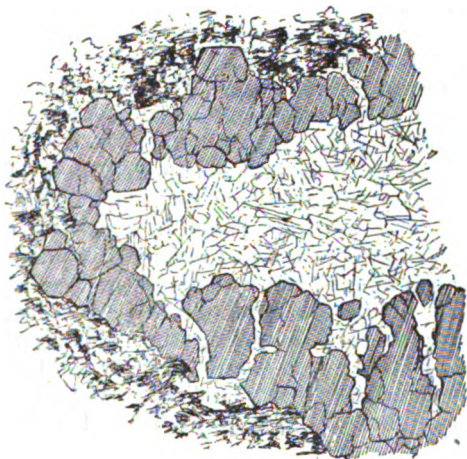
† It may be interesting to mention that a glaucophane-eclogite is far from uncommon in the boulders of the Saasthal. Here the mineral is richly coloured. I have not found the rock *in situ*, but have no doubt it is from some part of the range which extends from the Strahlhorn to the Egginerhorn. Most of this is a green schist with garnet, hornblende, &c and it contains, certainly sometimes, probably often, glaucophane.



from enclosures, but it occasionally contains a few granules of opacite, or a grain or a cluster of granules of the honey-brown mineral described below. In one specimen the edges of the crystals are sometimes fringed with a rather fibrous, distinctly green hornblende, indicating a change to which attention has often been called by writers on glaucophane-rocks.

The garnets, where they occur (they are present in both the above-named specimens containing glaucophane), are sometimes roundish grains, sometimes fairly idiomorphic\*, a pale straw-colour with a tinge of red, often so full of enclosures as to have a "dusty" aspect, but sometimes with clear parts. Some of these enclosures resemble films, and are doubly refracting, being possibly one of the constituents of the "saussurite." In one of the specimens the garnets are arranged in a kind of ring about the patches of glaucophane; the latter, however, occasionally interposes between them and the "saussurite" (fig. 1). This ring-like arrangement of the garnets is perceptible in the hand-specimen†.

Fig. 1. ( $\times 15$ . The garnet is shaded obliquely.)



Lastly, in both these specimens, and less abundantly in some of the others, we find a mineral, which occurs in grains and sometimes in prisms of a rich honey-brown, darkened in parts so as to become locally almost opaque. Very possibly

\* In one case the arrangement suggests that a larger grain has been broken up.

† Collected from a boulder between Zmeiden and the base of the Hochlaub glacier.

it is pseudobrookite\*. Characteristic microliths of rutile are occasionally present.

I have thought it needless to examine microscopically one of the specimens where the pyroxenic constituent is diallage, for macroscopically it is an ordinary gabbro, with the felspar considerably and the diallage slightly altered. I cannot detect any olivine, but this mineral occurs in the gabbro of Mont Colon†. Here the pyroxene changes into a rich green hornblende, as it also does (though, if my memory be correct, the colour is a little paler) in the gabbro mass on the west flank of the Matterhorn. I do not remember to have seen smaragdite at either of these localities; probably its occurrence in the Saasthal mass is due to some slight accidental difference in chemical composition‡.

Among the boulders was one resembling a dark greenstone in which were scattered a few fairly conspicuous crystals of smaragdite. Under the microscope it appears to be composed of saussurite and various pyroxenic and hornblendic constituents, much as above described (without glaucophane), but very confusedly mingled; the only well-defined mineral being small garnets with "dusty" centres and generally rounded outlines. It is quite possible that the constituents may have been crushed up together; but, if so, the last-named either have escaped or are later in date. There are also a few well-formed flakes of white mica, and sometimes (as observed by Dr. Sterry Hunt) a small quantity of talc.

It follows from what is said above that most of the constituents in these euphotides are of secondary origin; and the rock is the result of mineral change in a coarsely crystalline gabbro which originally consisted mainly of a plagioclase felspar, such as labradorite, and a diallage (or possibly augite). It is difficult to determine whether the garnets are original constituents of the rock or not, for the evidence appears to me rather conflicting; this may be due to the fact that the Alps have been subject to disturbance at more than one epoch; perhaps it is on the whole more probable that they also are secondary.

\* This mineral is frequent in the glaucophane eclogites. It is that noticed by myself, as probably impure sphene or rutile, in the rock from the Val d'Aosta (Min. Mag. vol. vii. p. 3), and by Mr. Rutley, Quart. Journ. Geol. Soc. vol. xlv. p. 61.

† See the author, "On some Specimens of Gabbro from the Pennine Alps," Min. Mag. vol. ii. p. 5.

‡ Dr. Sterry Hunt ('Contributions to the History of Euphotide,' &c.) found in the Saasthal smaragdite 61 of  $\text{Cr}_2\text{O}_3$ , with traces of nickel and even of cobalt. This may be the cause of the peculiar colour.

We may now pass on to inquire to what cause the slight foliation, commonly perceptible in one variety of this rock (No. 4), should be attributed.

The smaragdite-euphotide, it may be remarked, is a rock of exceptional hardness and toughness, breaking, apparently, with equal difficulty in all directions; but the variety of which we speak is not quite so intractable, and is occasionally, though not always, more fissile in the direction of its streaking. But, so far as I have observed, we do not find any surfaces of markedly imperfect cohesion, such, for instance, as are common in the "augen-gneisses." A careful, and I hope unprejudiced, examination of the smaragdite-euphotide blocks convinced me that they fail to reveal any conspicuous marks of "dynamo-metamorphism." In many, notwithstanding the changes each constituent has undergone, an ophitic structure on a large scale is still quite clear. The more granular varieties, whether coarser or finer, resemble the more granular types of ordinary gabbro.

Here it may be well to describe in some detail two or three examples, which appeared to me to give important evidence as to the history of the rock. First of these is one, which, at the first glance, might be supposed favourable to the idea of dynamo-metamorphism. It is a large block (about 6 feet by 3½ and at least a yard thick), consisting of saussurite and a dull green, almost dark-slate-coloured hornblende, which is slightly more porphyritic in aspect than is usual, crystalline grains of "saussurite" about 1 inch or 1.25 inch long occurring in a mass where they ranged downwards from about 5 inch. These larger crystals have a rather irregular outline. They are not, however, oval as in "augen-gneiss," but the ends are a little ragged or "teased" out, the smaller being more streak-like (fig. 2). Thus the rock exhibited a slight foliation, but was not in the least fissile parallel with it; the structure in short to my eye suggested fluxional movement prior to solidification rather than a crushing of a mass already solid. Here and there smaragdite comes in, grains of it being associated with and apparently replacing the dark-bluish (hornblendic) mineral. These grains occur in cloudlike streaks or veins, which have a slight tendency to run parallel with the structure of the rock.

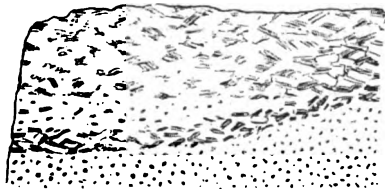
Fig. 2.



Another large block, the face of which was about 5 feet wide by 3 feet high, which lies some distance farther up the valley, also affords important evidence. At the top is a band, about 6 inches high, of a coarse gabbro, containing both smaragdite

and diallage (fig. 3). In parts of this, especially in the pyroxenic constituent, a slight "streakiness" is exhibited, in others an

Fig. 3.—Rough sketch of block showing a coarse gabbro streaking smaragdite-euphotide. The upper band is about 5 inches thick.



ophitic structure can be traced. In this the "crystals" of saussurite are sometimes 2.5 or 3 inches long; the patches of the pyroxenic mineral being even as much as 4 inches. The one form shades off into the other by imperceptible changes, the crystals of saussurite tending to assume a parallel position and to become, as it were, distorted. This coarse and slightly "orientated" band on the right-hand side of the block changes with great rapidity into a rather fine-grained, less pyroxenic variety of euphotide; the diameter of the pyroxenic constituents being about .25 inch at most, that of the saussurite a very little more. The structure of this rock is granular, and only here and there we detect a slight streakiness. But on the left-hand side of the block, as shown above, we find a band, about half a yard long and three inches broad, of a gabbro as coarse as that of the upper zone, and exhibiting in its crystals a similar, perhaps a shade more marked, tendency to orientation. The one is separated from the other by a band like the main mass of the block, though a little coarser and more pyroxenic, but at last the lower one "streaks" upwards to the upper. There is no sign that the one variety either has been made by a local crushing of the other, or is intrusive into it; but we observe a rapid transition from the one to the other, as in a rock which originally consisted of two magmas slightly different in composition.

Boulders are common in which there is a streaking or veining, without absolutely sharp boundaries, of finer varieties by coarser, or of those which are more felspathic by a rock richer in a pyroxenic constituent—augite, hornblende, or smaragdite.

Boulders also may be found occasionally in which bands of compact greenstone cut across the streaky structure in a euphotide, so as to prove that, whatever might be its cause, this structure existed at the time of the intrusion of the greenstone.

Yet this region, as a whole, undoubtedly has been subjected to very severe pressure, of which frequently there are conspicuous indications—for in some places serpentine has been crushed into a slaty schist, other rather less basic rocks into chloritic or hornblendic schists, granitoid rocks into slabby gneisses with “sheen surfaces,” &c.\*

Still, among these euphotides, certain specimens of those containing green hornblende (No. 4) present structures which make it possible that the mass was somewhat modified by crushing. This is the case with the small specimen from the spur of the Allaleinhorn, given to me by Mr. Eccles; also, though to a less extent, in sundry specimens collected by myself, one from the ridge, another from one of the bosses. But in the majority of the boulders of this type I could find no direct evidence in favour of their slight “flaser” structure being due to this cause, while occasionally their structures seemed readily explicable by fluxional movements, as is the case with certain of the gabbros at the Lizard. Hence, while I should admit that this euphotide had been occasionally modified by subsequent pressure, I should infer that on the whole it has done little more than modify structures which were original, and that these have been generally unaffected by the process of mountain-making.

From these observations it follows indirectly that gabbro is by no means a promising subject for “dynamo-metamorphism,” and to attribute a *flaser* structure to this agency, when no mark has been left on neighbouring and less obstinate rocks, is to quit induction for hypothesis†.

Two other matters, in connexion with these boulders, appear to me to call for a few remarks in conclusion:—

(a) In all parts of the Saasthal which I have examined, the boulders containing smaragdite are more abundant than those in which the dull green hornblende dominates (4). But, as I have stated, this is not the case on the ridge itself. The smaragdite, no doubt, may occur in parts which I did not see, as it does on the crags below the eastern end, but on the crest

\* The “cleavage foliation” is often so marked that the slabs are used for flooring and occasionally even for roofing.

† I have seen statements in print so worded as to suggest that a “uralitization” or conversion of augite into hornblende is *indicative* of “dynamo-metamorphism.” It is true that, as augite is a less stable mineral than hornblende, any disturbing agency is likely to set up the change from one condition to another, and so very often it results from dynamo-metamorphism, but I have found instances of this change when there was not the slightest indication of mechanical disturbance to be seen in the neighbourhood. Geologists would do well to remember that though A causes B, B is not always caused by A.

and for some distance below it the latter rock is certainly much the more abundant\*. The euphotide certainly is the more durable rock, but I do not think that a "survival of the fittest" is a sufficient explanation, and can only suppose that the smaragdite-euphotide predominated in the part of the mass which has been removed.

(b) The second matter seems to me a still greater difficulty. These blocks occur in countless thousands. To speak only of the valley above Saas-im-grund, the part which I have examined most closely, they abound in every wall, and are strewn thickly over many acres of land by the side of the torrent. It is, I believe, no exaggeration to say that they constitute one fourth of the boulders; often 3 or 4 may be seen actually touching one another; not seldom their volume is 2 or 3 cubic feet, often much more than a cubic yard. But, as I have already indicated, the parent mass of rock is rather small. Its surface, compared with that of the ridges and crags which pay tribute to the Hochlaub, Allalein, Schwarzenberg, and other glaciers is almost insignificant. An explanation might be suggested on the principle that "you cannot spend and have;" the gabbro mass may have impoverished itself by a lavish distribution of boulders, so that what we now see may be only a residual fragment of the original ridge. Such an answer, however, in reality increases rather than removes the difficulty. These boulders for the most part were distributed when the Alpine glaciers were much larger than at present. Add only fifty feet to the thickness of the *névé*, and the height of the ridge would be seriously diminished, while the two small neighbouring outcrops would, I believe, be buried. But the form of the ridge is such that there are difficulties in understanding how the height could be materially increased. It is like a wedge resting on the broader end, the crest being at most only a few feet wide, and its craggy sides are everywhere rather steep. It is my impression (and this accords with the map) that the greatest breadth of the base does not exceed a hundred yards. It would be difficult to pile up more than about ten thousand cubic yards of rock upon the present mass, yet the volume of the scattered blocks must greatly exceed this†.

\* I infer from Capt. Marshall Hall's account that there was at any rate a considerable quantity of the hornblende variety in the eastern crags.

† It might be suggested that the ridge was once longer and that the front part has been removed by denudation; but if so, and if the removal was effected when the glaciers were larger, we ought now to see a low spur exposed—the foundation of the portion removed—rising above the ice at the base of the crag at the eastern end.

But the blocks may also be traced up the slopes some height above the bed of the Saasthal\* and are carried down the valley of the Rhone to beyond Geneva, though of course they become much less numerous in the lower part, even of the Vispthal. If, however, the glaciers extended only as far as Stalden, at least a considerable portion of the ridge would be concealed, and during no small fraction of the Ice Age it must have been completely buried. In my opinion, we are not materially helped by assuming that a large area of gabbro may be buried beneath the present glaciers†; for I am not aware of any evidence which would justify us in assuming that masses of rock can be, to any great extent, gripped and torn off by the lower part of a glacier and then transported beneath the ice. At the present time, as probably at all times, most boulders of any size begin their journey on the surface of the glacier, i. e. have fallen upon it from crags. Is it possible that, during a long period anterior to the "Great Ice Age," the Alpine glaciers either were much smaller than they are at present, or perhaps had entirely disappeared? As I have elsewhere shown‡, a rise of only 6° F. in the mean temperature of Switzerland would suffice to remove them from many districts and reduce them, even in this part of the Pennines, to comparative insignificance. If so, blocks doubtless might be accumulated by the ordinary processes of mountain destruction over an area much more extensive than is now exposed, and these might be gradually swept onwards by the advancing ice. Some of these also must have been lifted vertically, for, as I have said, they occur at least 500 feet above the bed of the Vispthal. But even this hypothesis does not appear to me to remove the difficulty, for where the boulders are most abundant they lie as if they had been dropped during the retreat of the ice. So we must suppose that the glacier kept depositing them on the bed of the valley and then over-riding them: a process which I find not very easy to understand, and one which, if acknowledged, would be extremely difficult to reconcile with that excavating power

\* I have only seen them up to 500 or 600 feet above the river, but very likely they go higher. I have not had a good opportunity of searching for and determining their vertical range.

† At the lower end of the ridge we appear to be approaching the inferior limit of the mass, for Mr. Eccles informs me that in 1890 he saw (but could not actually touch) a dark green rock (either serpentine or the "green schist" of the district) below the euphotide and above the surface of the glacier. The ridge does not appear at the present time to give rise to any well-marked moraine.

‡ "The Growth and Sculpture of the Alps," 'Alpine Journal,' vol. xiv. p. 233.

which is almost an axiom with some glacialists\*. In short, I have not been able to find any thoroughly satisfactory solution of the difficulty,—a difficulty which is not without precedent elsewhere†. For the present I must be content to state it, and let it remain among the riddles in which the Glacial Epoch is so fruitful.

XXV. *On the Theory of Long Waves and its Application to the Tidal Phenomena of Rivers and Estuaries.* By J. McCOWAN, M.A., B.Sc., Assistant Lecturer on Natural Philosophy, University College, Dundee‡.

THE theory of the long wave has received considerable attention since the time of Lagrange, who obtained the well-known first approximation for its velocity in a channel of uniform rectangular cross section§. In 1839 Green|| obtained the corresponding result for a channel of triangular section, and Kelland¶ that for a channel of any uniform section. So far, however, only the first approximation had been discussed. Sir George B. Airy, in his treatise on "Tides and Waves" in the *Encyclopædia Metropolitana* (1845), gave for the first time, so far as I am aware, the exact equation on which the theory of the long wave in a channel of uniform rectangular section depends: he gave no general solutions, but discussed certain problems very fully by methods of approximation\*\*. I do not know that any advance on Airy's treatment has since been published. The subject is briefly discussed in Prof. G. H. Darwin's article on "Tides" in the *Encyclopædia Britannica* (ninth edition), but only an abstract of Airy's results is given.

In the following paper I have sought to give a fairly complete discussion of the motion of long waves in a channel of any uniform section, but I have not sought to consider channels of varying section. For the case of waves propa-

\* It must be remembered that here we are among the mountains in a locality where the excavating powers of the glaciers should be at a maximum; so the difficulty cannot be eluded by the analogy of a stream which will excavate where the descent is rapid and deposit where this is gentle.

† *Quart. Journ. Geol. Soc.* 1835, p. 514.

‡ Communicated by the Author.

§ *Berlin Memoirs*, 1786.

|| *Trans. Camb. Phil. Soc.* vol. vii.

¶ *Trans. Roy. Soc. Edinb.* vol. xiv.

\*\* An interesting account of Airy's results is given by Stokes in his "Report on Recent Researches in Hydrodynamics," B. A. Reports, 1846.



gated in one direction only the complete solution is given, and the general solution for propagation in both directions is obtained in finite terms for a system of different forms of channel. One of these forms of channel is peculiarly interesting in respect of the fact that long waves of any kind are propagated along it without change of form : in all other forms of channel long waves change in form as they advance. For such a channel, which may be called a channel of uniform propagation, the general solution takes a specially simple form, and I have devoted a section to its discussion.

Perhaps the most important application of the theory is to the explanation of the tidal phenomena of rivers and estuaries. In the treatise on "Tides and Waves" the application was made by Airy with great success. As, however, the results were obtained from approximations only, I have thought it desirable to re-discuss some of them with the aid of the exact solutions. As was to have been expected, they are, so far as they go, confirmed in the main ; but one of them, to which some importance has been attached, is found to be erroneous. I refer to the explanation of what are called double tides, sometimes observed in rivers at stations sufficiently far from the mouth. The splitting up of the wave, however, indicated by Airy's solution, and on which the explanation depended, is only apparent and depends on the fact that the approximation used is not sufficiently exact for stations far up the river : in the exact solution there is no trace of such a division.

### 1. *The Equations of Motion.*

Consider a canal or horizontal channel of any uniform cross section filled initially to a certain depth with water or other liquid. Suppose that this liquid is now disturbed in such a way that all particles which are initially in any horizontal or vertical straight line perpendicular to the length of the channel receive a common horizontal displacement and are then left free with a common velocity parallel to the length of the channel, the displacement and velocity, however, being such that the inclination of the path of any particle to the length of the channel is everywhere very small and the motion continuous. Such a disturbance will in general give rise to a wave-motion in which "long waves" with parallel crests are propagated in both directions along the channel. The nature of this motion we proceed to investigate.

Taking the axis of  $x$  parallel to the length of the channel, along its bottom say, let  $\xi$  be the abscissa at time  $t$  of a plane perpendicular to this axis containing a set of particles which,

before the liquid was disturbed, had the common abscissa  $x$ . Let  $z$  denote the height of the free surface of the liquid above the axis of  $x$ , where it is cut by the plane  $\xi$ , and let  $h$  be the undisturbed height. Since the form of the cross section of the channel is supposed given, the area of the section of the liquid made by the plane  $\xi$  is a function of  $z$  which can be determined and may therefore be supposed known, say  $\phi(z)$ , and the area of the undisturbed section being the same function of  $h$  must therefore be  $\phi(h)$ .

Consider now two planes, perpendicular to the length of the channel, which move with the fluid and so contain always the same particles, and which, before the liquid was disturbed, were at the small distance  $\delta x$  apart: at time  $t$  their distance apart will have become  $\delta \xi = \delta x \cdot d\xi/dx$ , but the quantity of liquid between them will be unaltered and therefore  $\phi(z)\delta \xi = \phi(h)\delta x$ , or

$$\frac{d\xi}{dx} = \frac{\phi(h)}{\phi(z)}. \quad \dots \dots \dots (1)$$

This is the "equation of continuity," and we have also, if  $u$  denotes the component of the velocity parallel to the axis of  $x$ ,

$$\frac{d\xi}{dt} = u. \quad \dots \dots \dots (2)$$

Next, let  $\rho$  be the density of the liquid and let  $p$  be the pressure at any point on the plane  $\xi$ : the motion, parallel to the axis of  $x$ , of the particles near this point will therefore be given by the dynamical equation

$$\rho \frac{d^2 \xi}{dt^2} = - \left( \frac{dp}{d\xi} \right);$$

or, by (1),

$$\rho \frac{d^2 \xi}{dt^2} = - \frac{\phi(z)}{\phi(h)} \frac{dp}{dx}. \quad \dots \dots \dots (3)$$

Now, from the initial conditions, it is clear that the vertical component of the acceleration will be negligible, and therefore that the variation of the pressure from point to point will be due entirely to the variation in the depth below the surface: thus, for points on the same horizontal plane,  $\delta p = g\rho \delta z$ , and therefore (3) gives

$$\frac{d^2 \xi}{dt^2} = -g \frac{\phi(z)}{\phi(h)} \frac{dz}{dx}. \quad \dots \dots \dots (4)$$

Thus the component of the acceleration parallel to the axis of  $x$  is the same for all the particles in any plane  $\xi$  perpendicular to the length of the channel, and therefore all particles

initially in such a plane will remain so, having a common horizontal velocity.

If, finally, we differentiate (4) with respect to  $x$ , we get by (1),

$$\frac{d^2 \phi(h)}{dt^2 \phi(z)} = -g \frac{d \phi(z)}{dx \phi(h)} \frac{dz}{dx};$$

or

$$\frac{d}{dt} \left( \frac{\phi(h)}{\phi(z)} \right)^2 \phi'(z) \frac{dz}{dt} = \frac{d}{dx} g \phi(z) \frac{dz}{dx}. \quad \dots (5)$$

The particular case in which the cross section of the channel is rectangular is specially important. Here  $\phi(z)$  is proportional to  $z$ , and therefore the equations (1) to (5) reduce to

$$\frac{d\xi}{dx} = \frac{h}{z}. \quad \dots (1')$$

$$\frac{d\xi}{dt} = u. \quad \dots (2')$$

$$\frac{d^2 \xi}{dt^2} = -\frac{z}{h} \frac{dp}{dx}. \quad \dots (3')$$

$$\frac{d^2 \xi}{dt^2} = -g \frac{z}{h} \frac{dz}{dx}. \quad \dots (4')$$

$$\frac{d}{dt} \frac{h^2}{z^2} \frac{dz}{dt} = \frac{d}{dx} g z \frac{dz}{dx}. \quad \dots (5')$$

Equations (1) to (5), with the initial and boundary conditions, completely determine the motion. It is, however, very necessary to use great care in interpreting these equations, remembering that they are subject to the limitations assumed in obtaining them. We shall see later that though the initial circumstances of the motion satisfy these conditions, still the motion will gradually alter in character till they are no longer fulfilled, and therefore the further motion will not be given by these equations. It is therefore important to note clearly what are the fundamental conditions to be satisfied in order that any wave-motion may be included in the theory of long waves.

The essential feature of the theory is the motion in parallel sections; that is, the motion must be such that all particles initially in a plane, perpendicular to the length of the channel, remain in such a plane. The investigation shows that the motion will have this character provided that initially all particles in such planes receive a common displacement and

*Phil. Mag. S. 5. Vol. 33. No. 202. March 1892. T*

velocity parallel to the length of the channel, great in comparison with the other two components of the displacement and velocity. It is clear that this imposes a certain limitation on the form of the cross section of the channel: near the surface the inclination of the sides to the vertical must not be so great as to occasion too great a transverse motion, as the surface rises and falls between wave-crest and hollow. In obtaining (4) the exact assumption made is that the vertical component of the acceleration of any particle is very small in comparison with the free acceleration  $g$  due to gravity.

As an example, suppose that the form of the surface is given by a curve of sines or similar curve. Then it is clear that, to satisfy the conditions, the height of the waves, and the variation in the breadth of the channel between wave-crest and trough, must be very small in comparison with the length of the wave; and it may also be seen without much difficulty that the ratio of the wave-height to the wave-length must be large compared with the square of the ratio of the depth to the wave-length.

## 2. *The Propagation of Waves in one Direction only:* *General Solution.*

The most important problems in wave-motion are those in which waves are propagated in one direction only. When this limitation is imposed, the complete solution of the problem of the propagation of long waves may be obtained as follows:—

Let  $\alpha$  and  $\beta$  be functions of  $z$ , as yet undetermined; assume for a unidirectional solution,

$$z = F_0(x - \alpha t).$$

This gives

$$\frac{dz}{dt} = -\alpha \frac{dz}{dx},$$

and therefore further

$$\frac{d}{dt} \beta \frac{dz}{dt} = \frac{d}{dx} \alpha^2 \beta \frac{dz}{dx},$$

which will become identical with (5), if we take

$$\beta = \left( \frac{\phi(h)}{\phi(z)} \right)^2 \phi'(z), \text{ and } \alpha^2 \beta = g\phi(z),$$

which gives

$$\alpha = \pm \frac{\phi(z)}{\phi(h)} \sqrt{g\phi(z)}.$$

The double sign has only reference to the direction of propagation of the waves, and we shall therefore obtain sufficient

generality by taking the upper sign only. The complete solution of (5) for an advancing series of waves of any form is therefore given by

$$z = F_0 \left( x - t \frac{\phi(z)}{\phi'(h)} \sqrt{g \frac{\phi(z)}{\phi'(z)}} \right), \dots \quad (6)$$

where  $z = F_0(x)$  when  $t = 0$ . Here the ordinate of the surface at any time  $t$  is given for the plane of particles whose abscissa in their undisturbed position was  $x$ , and we may obtain from this  $\xi$ ,  $u$ , and  $p$  by means of equations (1), (2), and (3). As, however, it is generally more convenient and shows the character of the motion more clearly, to have all quantities given in terms of the actual abscissa  $\xi$  at time  $t$ , rather than the abscissa  $x$  corresponding to an anterior undisturbed condition, we shall work out the results in this form.

Using the letter  $F$  with various suffixes to denote a series of functions related to  $F_0$  in ways which will be sufficiently obvious from the transformations without other explanation, (6) may be written

$$x = F_1(z) + t \frac{\phi(z)}{\phi'(h)} \sqrt{g \frac{\phi(z)}{\phi'(z)}},$$

and therefore by (1)

$$d\xi = \frac{\phi(h)}{\phi(z)} dx = \frac{\phi(h)}{\phi(z)} dF_1(z) + t \frac{\phi(h)}{\phi(z)} d \cdot \frac{\phi(z)}{\phi'(h)} \sqrt{g \frac{\phi(z)}{\phi'(z)}};$$

$$\therefore \xi = F_2(z) - kt + t\psi(z) \sqrt{g},$$

where

$$\psi(z) = \int \left\{ \frac{3}{2} \sqrt{\frac{\phi'(z)}{\phi(z)}} - \frac{1}{2} \frac{\phi''(z)}{\phi'(z)} \sqrt{\frac{\phi(z)}{\phi'(z)}} \right\} dz, \quad (7)$$

and  $kt$  is written in place of the arbitrary function of  $t$  which would naturally appear on integration, for we easily find on substitution in (4) that this function reduces to the form  $kt$ ,  $k$  being an absolute constant. Thus, finally,

$$z = F \{ \xi - (\sqrt{g} \cdot \psi(z) - k)t \}, \dots \quad (8)$$

where  $z = F(\xi)$  is the equation to the wave-form when  $t = 0$ .

Again,

$$u = \frac{d\xi}{dt} = \frac{d\xi}{dz} \frac{dz}{dt} + \sqrt{g} \cdot \psi(z) - k.$$

Also

$$\frac{\phi(h)}{\phi(z)} = \frac{d\xi}{dx} = \frac{d\xi}{dz} \frac{dz}{dx} = - \frac{d\xi}{dz} \frac{\phi(h)}{\phi(z)} \sqrt{\frac{\phi'(z)}{g\phi(z)}} \frac{dz}{dt};$$

$$\therefore \frac{d\xi}{dz} \frac{dz}{dt} = - \sqrt{\frac{g\phi(z)}{\phi'(z)}}.$$

Thus

$$u = \sqrt{g} \left\{ \psi(z) - \sqrt{\frac{\phi(z)}{\phi'(z)}} \right\} - k. \quad (9)$$

For the case of a channel of rectangular section, equations (6) to (9) reduce to

$$z = F_0(x - tz^{\frac{1}{2}}/h), \quad (6')$$

$$\psi(z) = 3\sqrt{z}, \quad (7')$$

$$z = F \{ \xi - (3\sqrt{gz} - k)t \}, \quad (8')$$

$$u = 2\sqrt{gz} - k. \quad (9')$$

Equations (7) to (9) supply immediately the solution of two very important general problems. Thus, if we are given the form of the surface, say  $z = F(\xi)$ , of a train of waves advancing in a channel of given uniform cross section at any time, which may conveniently be taken as zero, the form of the surface at any subsequent time  $t$  will be given by (7) and (8), and the velocity  $u$  by (9). Again, if a procession of waves is propagated along the channel by imposing a forced motion, say  $z = f(t)$ , at some part of the channel, which may conveniently be taken as the origin, then the form and motion generally of the advancing waves will again be given by the equations (7) to (9), (8) being modified to the form

$$z = f \{ t - \xi / (\sqrt{g} \cdot \psi(z) - k) \}, \quad (10)$$

or

$$z = f \{ t - \xi / (3\sqrt{gz} - k) \}, \quad (10')$$

if the section is rectangular.

In both these solutions it will be seen that the constant  $k$  is left undetermined; by (9) we see that it will be determined by the consideration of the normal velocity of flow in the channel independent of the wave-motion. Thus, if when no waves are being propagated along the channel, there is a uniform flow in it in the direction of the axis of  $x$ , the velocity being  $U$ , then, if we regard the wave-motion as such as not in itself producing a permanent flow, we must have

$$UT = \int_0^T u \, dt$$

when the time  $T$  is taken sufficiently long.

Thus, by (9),  $k$  will be determined by the condition

$$kT = \int_0^T \sqrt{g} \left\{ \psi(z) - \sqrt{\frac{\phi(z)}{\phi'(z)}} \right\} dt - UT, \quad (11)$$

where  $T$  is very large. In the case of rectangular section this reduces to

$$kT = \int_0^T 2\sqrt{gz} dt - UT. \quad (11')$$

In a subsequent section a discussion of some of the tidal phenomena of rivers and estuaries will afford a somewhat detailed illustration of the character of the motion which is indicated by the equations we have obtained in this section; but meanwhile a brief sketch of its general nature is desirable.

From (8) we see that any point on the wave-surface whose ordinate is  $z$  may be regarded as advancing without change of elevation with the velocity  $(\sqrt{g\psi(z)} - k)$ ; thus in general the waves will change in form as they advance, owing to the difference in the velocities of higher and lower parts, becoming steeper or less steep in front according as  $\psi(z)$  increases or decreases as  $z$  increases, but they will be propagated with a constant velocity and without change of form if  $\psi(z)$  is constant, a case to be specially discussed in the next section. From (8) we also see that though the form may change, the height of the wave-crests and troughs does not alter. From (9) we see that at any point the component of the velocity parallel to the axis of  $x$  depends only on the surface-height at the point; the vertical component of the velocity will of course be  $dz/dt$  at the surface, and, since it vanishes at the bottom, it will for intervening points be proportional to their height above the bottom.

An important consequence of the continual change in the form of the advancing wave must here be noted. As the velocity of advance of each point of the wave-surface depends only on its ordinate and not at all on the time, it follows that, the case where  $\psi(z)$  is a constant alone being excepted, the inclination at some points on the surface, however small initially, will ultimately become so great that the conditions under which our equations have been obtained no longer hold there. It follows, therefore, that we must be careful only to apply our results throughout those regions and during those times in which the condition of small surface-inclination holds, and we must infer nothing as to the further motion without special investigation. It seems to be generally held that the distortion of the surface-form will go on till discontinuity results; but such an inference can hardly rest on secure grounds so long as no equations are known which will represent even approximately the motion when the steepness of the surface becomes considerable; on the contrary, from the known fact of the permanent propagation of certain forms

of steep waves, it seems more probable that the ultimate fate of the waves will depend entirely on the initial circumstances.

### 3. The Channel of Uniform Propagation.

The solution of the problem of the propagation of long waves in one direction only which we have obtained affords little or no clue to the treatment required for the general case of propagation in both directions. The complete solution of this latter problem in finite terms is in general unattainable; but, as we shall see immediately, there is an infinite variety of forms of cross section for which such solutions may be obtained. Of these forms of section, however, there is one which, from its special interest and simplicity, deserves a separate discussion.

From the form of equation (5) we see that it will reduce to

$$\frac{d^2 \phi(h)}{dt^2} = gc \frac{d^2 \phi(z)}{dx^2},$$

or by (1) to

$$\frac{d^2 \xi}{dt^2} = gc \frac{d^2 \xi}{dx^2}, \quad \dots \quad (12)$$

if we take  $\phi(z)$  such that

$$\left\{ \frac{\phi(h)}{\phi(z)} \right\}^2 \frac{\phi'(z)}{\phi(z)} = \frac{1}{c},$$

which gives on integrating

$$\left\{ \frac{\phi(h)}{\phi(z)} \right\}^2 = 1 - 2(z-h)/c. \quad \dots \quad (13)$$

Let  $y$  denote the breadth of the cross section corresponding to the ordinate  $z$ , let  $b$  denote the breadth at the mean level  $h$ , and let  $A$  be written for  $\phi(h)$ , the area of the mean cross section. Then, by (13),

$$\phi(z) = A/\{1 - 2(z-h)/c\}^{\frac{1}{2}}; \quad \dots \quad (14)$$

$$\therefore y = \phi'(z) = A/c\{1 - 2(z-h)/c\}^{\frac{1}{2}}; \quad \dots \quad (15)$$

$$\therefore b = \phi'(h) = A/c,$$

$$\text{or} \quad c = A/b. \quad \dots \quad (16)$$

The complete solution of (12) is

$$\xi = f_1(x - Vt) + f_2(x + Vt), \quad \dots \quad (17)$$

where

$$V = \sqrt{gc} = \sqrt{(gA/b)}; \quad \dots \quad (18)$$



and this gives by (1) and (14)

$$\{1 - 2(z-h)/c\}^{\frac{1}{2}} = f_1'(x-Vt) + f_2'(x+Vt), \quad (19)$$

and by (2)

$$u/V = -f_1'(x-Vt) + f_2'(x+Vt). \quad (20)$$

From (17) we see that the most general motion in a channel of such a cross section as is given by (15) may be regarded as compounded of two series of waves of horizontal displacement moving in opposite directions with equal constant velocities. The constant velocity  $V$  given by (18), and here appearing as an exact result, is of the same form as Kelland's well-known approximation for the mean rate of propagation in a channel of any section, which latter result may of course be derived immediately from (5). From (16) it may be noted that the constant  $c$  is the average depth over the cross section. If we consider the solution obtained by taking only one of the arbitrary functions in (17) and (18), we see that it represents a propagation of waves in one direction only, with a constant velocity and without change of form; hence a channel with such a cross section as we are considering may be called a channel of uniform propagation. It is obvious, moreover, that it is only that part of the section which lies between the highest crest and lowest trough that need have the form given by (15), provided the section below this level is still such as to make the area equal to  $A$ . Thus, any channel may be made a channel of uniform propagation by suitably sloping the sides between the levels of crest and hollow of such waves as traverse it, provided always of course that the slope required be not such as to imply a greater transverse motion than is contemplated in the formation of the fundamental equations (1) to (5). If  $\theta$  denote the required inclination of each of the two sides to the vertical, corresponding to the ordinate  $z$ , taking for simplicity the case of equal slope on each side, then by (15)

$$2 \tan \theta = \phi''(z) = 3A/c^2 \{1 - 2(z-h)\}^{\frac{1}{2}}, \quad (21)$$

and, if  $\theta_0$  be the inclination at the mean level  $h$ ,

$$2 \tan \theta_0 = 3A/c^2 = 3b^2/A. \quad (22)$$

The equation to the form of the disturbed surface at any time  $t$  will be obtained explicitly by eliminating  $x$  between (17) and (19), but generally it will be more convenient to leave  $x$  uneliminated, regarding it rather as a variable parameter. It is important to notice that, though waves advancing in one direction only are propagated unchanged, in the general case the form of the surface cannot be obtained by simply

superposing the forms of the two oppositely moving systems of waves of which it may be regarded as the result. It is clear, however, from (17) that the displacement of any plane from its mean or undisturbed position is simply the sum of the displacements due to the component waves.

#### 4. A General Solution: Solutions in Finite Terms.

The solution which has just been discussed is the simplest of a series of complete solutions in finite terms which may be obtained for a corresponding series of forms of cross section. For if we take  $\phi(z) = (a+bz)^n$ , then taking advantage of (1), (4) may be written

$$\frac{d^2\xi}{dt^2} = \frac{g(a+bh)}{nb} \frac{d^2\xi}{dx^2} \left| \frac{d\xi}{dx} \right|^{2+1/n}; \quad \dots \quad (23)$$

and if we change the independent variables in this to  $u = d\xi/dt$  and  $p = d\xi/dx$ , and the dependent variable to  $\mathfrak{S} = px + ut - \xi$ , we get

$$p^{2+1/n} \frac{d^2\mathfrak{S}}{dp^2} = \frac{g(a+bh)}{nb} \frac{d^2\mathfrak{S}}{du^2}; \quad \dots \quad (24)$$

an equation of a form which has received considerable attention, the equations of Riccati and Bessel being connected with it. The general solution of (23) will then be given by the following equations:—

$$\frac{d\xi}{dx} = \frac{\phi(h)}{\phi(z)} = \left\{ \frac{a+bh}{a+bz} \right\}^n, \quad \dots \quad (25)$$

$$x = -\frac{(a+bz)}{nb} \left\{ \frac{a+bz}{a+bh} \right\}^n \frac{d\mathfrak{S}}{dz}, \quad \dots \quad (26)$$

$$t = \frac{d\mathfrak{S}}{du}, \quad \dots \quad (27)$$

$$\left\{ \frac{a+bh}{a+bz} \right\}^n x + ut - \xi = \mathfrak{S}; \quad \dots \quad (28)$$

where  $\mathfrak{S}$  is the general solution of (24), which may be easily shown to be, on substituting for  $p$  its value in terms of  $z$ ,

$$\begin{aligned} \mathfrak{S} = & \int_0^\pi f_1(u - \sqrt{4ng(a+bz)}/b \cdot \cos \phi) \sin^{2n} \phi \cdot d\phi \\ & + \int_0^\pi f_2(u + \sqrt{4ng(a+bz)}/b \cdot \cos \phi) \sin^{2n} \phi \cdot d\phi. \end{aligned} \quad (29a)$$

when  $n$  is positive, and

$$\begin{aligned} \eta = & (a+bz)^{-n} \int_0^\pi f_1(u - \sqrt{4ng(a+bz)/b} \cdot \cos \phi) \sin^{-2n} \phi \cdot d\phi \\ & + (a+bz)^{-n} \int_0^\pi f_2(u + \sqrt{4ng(a+bz)/b} \cdot \cos \phi) \sin^{-2n} \phi \cdot d\phi, \quad (29b) \end{aligned}$$

when  $n$  is negative: if  $n$ , however, lies between  $+\frac{1}{2}$  and  $-\frac{1}{2}$  either form may be taken.

From this general solution we see immediately that if  $2n$  be an odd integer, positive or negative, the solution will take a finite form on integrating. We shall obtain, in fact,

$$\begin{aligned} \eta = \frac{d^i}{dz^i} \{ & F_1(u - \sqrt{2g(2i-1)(a+bz)/b}) \\ & + F_2(u + \sqrt{2g(2i-1)(a+bz)/b}) \}, \quad . \quad . \quad (30) \end{aligned}$$

or

$$\begin{aligned} \eta = \left\{ \frac{a+bz}{a+bh} \right\}^{i-\frac{1}{2}} \frac{d^i}{dz^i} \{ & F_1(u - \sqrt{-2g(2i-1)(a+bz)/b}) \\ & + F_2(u + \sqrt{-2g(2i-1)(a+bz)/b}) \}, \quad . \quad . \quad (31) \end{aligned}$$

according as  $n = i - \frac{1}{2}$  or  $n = \frac{1}{2} - i$ ,  $i$  being a positive integer. These cases of finite solution are specially interesting for the smaller values of  $i$ , as being then more easily interpreted: it may be noted that the case of the channel of uniform propagation is obtained by taking  $i=0$ , in (30), or  $i=1$ , in (31). It should be observed that, as in any real channel the cross-sectional area  $\phi(z)$  must increase with  $z$ ,  $b$  and  $n$  must be quantities of the same sign.

Whatever be the form of  $\phi(z)$ , the general equation (4) might be treated by thus changing the independent variables to  $u$  and  $p$ ; but the solution would in general be very complex in form. This mode of solution, however, is interesting theoretically from its relation to the finite solution we have obtained for waves propagated in one direction only. For that solution is the most general one that satisfies the condition  $u=f(p)$ , while this latter is general only when  $u$  and  $p$  are independent; thus the solutions are supplementary to each other, the cases excluded from the one system are precisely those included under the other.

### 5. Tides in Rivers and Estuaries.

The tide in a river or long narrow estuary is due to the propagation upwards from the outlet of long waves which may be regarded as forced by the oceanic tide at the mouth. This tide at the mouth may, for our present purpose, be regarded as compounded of two simple harmonic constituents,

the lunar and solar semidiurnal tides; and if we do not seek to trace its variation from spring tide to neap, it will be sufficient to replace these, as their periods are roughly equal, by one, and take

$$\eta = \eta_0 \sin nt \quad . \quad . \quad . \quad . \quad . \quad (32)$$

as representing the oceanic tide at the river-mouth;  $\eta$  denoting the elevation of the surface above mean level, and  $n = 2\pi/T$  the "speed" of the tide, which has the period  $T$ . But if we want to consider the phenomena of spring and neap tides we must take

$$\eta = \eta_1 \sin n_1 t + \eta_2 \sin n_2 t; \quad . \quad . \quad . \quad . \quad (33)$$

where  $n_1$  and  $n_2$  are the speeds, and  $2\eta_1$ ,  $2\eta_2$  the ranges of the lunar and solar semidiurnals respectively.

Consider the case of a river or long narrow estuary which approximates in form to a straight channel of uniform rectangular section. Let the origin be taken at the mouth of the river, and let  $x$  be measured from the mouth up. Then if the oceanic tide at the river-mouth be given by (32), we see by (10') that, writing  $\eta$  for  $z - h$ , the elevation above mean level, the tide-wave propagated up the river in consequence will be given by

$$\eta = \eta_0 \sin n \{ t - \xi / (3 \sqrt{g(h + \eta)} - k) \}, \quad . \quad . \quad (34)$$

where  $k$  is a constant to be determined from the mean rate of efflux from the river. Thus if the natural velocity of the stream towards its mouth be  $q$ , then by (11'), noting that the integration need only extend over the period,

$$\begin{aligned} k &= q + \frac{1}{T} \int_0^T 2 \sqrt{g(h + \eta_0 \sin 2\pi t/T)} dt; \\ \therefore k &= q + \frac{\sqrt{g}}{\pi} \int_0^{2\pi} \sqrt{h + \eta_0 \sin \theta} . d\theta; \\ \therefore k &= q + \frac{4 \sqrt{g(h + \eta_0)}}{\pi} \int_0^{\pi/2} \sqrt{1 - \frac{2\eta_0}{h + \eta_0} \sin^2 \phi} . d\phi; \\ \text{or} \quad k &= q + \frac{4 \sqrt{g(h + \eta_0)}}{\pi} E \left( \sqrt{\frac{2\eta_0}{h + \eta_0}} \right). \quad . \quad . \quad . \quad (35) \end{aligned}$$

The limiting values between which  $k$  must always lie are therefore given by

$$k = q + 2 \sqrt{gh} \quad \text{when } \eta_0 = 0, \quad . \quad (36)$$

$$k = q + \frac{4\sqrt{2}}{\pi} \sqrt{gh} = q + 1.8 \sqrt{gh} \quad \text{when } \eta_0 = h; \quad . \quad (37)$$

so that in approximations the value given by (36) may generally be taken.

By means of these results we can easily see the chief characteristics of the tidal ebb and flow in such a river or estuary. From (34) it follows that the height of rise and fall is the same at all stations on the river as that of the oceanic tide at the mouth, but the rise and fall is not simple harmonic except at the mouth. We see also that high water occurs later at stations up the river than at the mouth, the lag, which is simply proportional to the distance from the mouth, being less for high than for low tides, and also less the less the natural flow in the river: the same is true for the time of low water, but the lag is greater and it is greater for high than for low tides; hence the interval from low water to the high water following is less than the interval from high water to the following low water. In fact, from (34), the interval from high water to the succeeding low water, at a station at distance  $\xi$  from the mouth, is

$$\frac{1}{2}T + \xi \left\{ \frac{1}{3\sqrt{g(h-\eta_0)}} - \frac{1}{3\sqrt{g(h+\eta_0)} - k} \right\}, \quad (38)$$

or approximately, taking  $k = q + 2\sqrt{gh}$  and neglecting  $\eta_0^2$ ,

$$\frac{1}{2}T + \xi \frac{3\sqrt{gh} \cdot \eta_0/h}{(\sqrt{gh} - q)^2}; \quad \dots \dots \dots (39)$$

and therefore, making the same approximations, the interval from low water to the following high water at the same station will be

$$\frac{1}{2}T - \xi \frac{3\sqrt{gh} \cdot \eta_0/h}{(\sqrt{gh} - q)^2}. \quad \dots \dots \dots (40)$$

From (39) and (40) it follows that the difference in the two intervals increases directly as the distance from the mouth and as the height of the tide approximately: it is also greater the greater the natural velocity  $q$  of the stream.

Again, by (9'),

$$u = 2\sqrt{g(h+\eta)} - k, \quad \dots \dots \dots (41)$$

whence it follows that the rate of flow is a maximum at high water, and the rate of ebb a maximum at low water. Also, flood ends and ebb begins, or *vice versa*, when

$$2\sqrt{g(h+\eta)} = k, \quad \dots \dots \dots (42)$$

and therefore at an elevation above mean level which is

greater the greater the natural stream-velocity  $q$ : when there is no stream-velocity  $q$  ebb will begin approximately at the mean level  $h$ , but really somewhat below this, and more notably when the tide is a high one.

Again, by (34) and (42), the duration of flood will be

$$\frac{1}{2}T - \frac{T}{\pi} \sin^{-1} \frac{\eta}{\eta_0}, \quad . . . . . (43)$$

where  $\eta$  is given by (42): therefore the duration of flood is approximately

$$\frac{1}{2}T - \frac{T}{\pi} \frac{q \cdot h/\eta_0}{\sqrt{gh}}, \quad . . . . . (44)$$

and that of ebb

$$\frac{1}{2}T + \frac{T}{\pi} \frac{q \cdot h/\eta_0}{\sqrt{gh}}. \quad . . . . . (45)$$

Thus the durations of flood and ebb are very nearly equal when there is no independent flow in the river, but the ebb continues longer than the flow when there is an independent flow  $q$  towards the sea, as was to be expected.

All these results are in complete accordance with the observed phenomena of the tides in rivers. Most of them, in their approximate form, were given by Sir George B. Airy in the article "On Tides and Waves," already referred to. His approximation, however, led him to the further result that the wave of the tide would subdivide as it advanced up the river, so that at stations far enough up there would be two times of high water in each period, or even three or more at sufficiently distant stations. As a matter of fact there is such a phenomenon of double tide in the upper parts of some rivers, and this result was therefore taken as its explanation: it is easy to see from (34), however, that there is really no such subdivision, and that therefore the explanation of such a peculiarity must be sought elsewhere. For (34) shows that each point on the wave-surface may be regarded as advancing up the river without change of elevation with a velocity  $[\frac{3}{2}\sqrt{(gz)} - k]$ , which depends only on its elevation, and which is greater the greater the elevation. Hence the slope at every point from the trough to the crest in front of the wave, which near the mouth has the form of a curve of sines, becomes greater, and at every point in the rear from crest to trough it becomes less. Thus we can easily picture, or draw if need be, the form of the advancing wave; but without this, however, the general considerations show that there can be no subdivision, even though the wave were traced up to the point

at which the equations indicate discontinuity, a point far beyond that permissible under the fundamental assumptions. It is clear, therefore, that the subdivision obtained by Airy must be due to his having extended his interpretation of his approximation to a distance at which it ceased to give a fair account of the motion. In fact, returning to (34), if we put  $n/\sqrt{gh}=m$ , take  $q=0$  and  $k=2\sqrt{gh}$ , we shall get at once for an approximation,

$$\eta = \eta_0 \sin (nt - m\xi - \frac{3}{2} m\xi \cdot \eta/h),$$

or

$$\eta = \eta_0 \sin (nt - m\xi) - \frac{3}{4} \cdot \eta_0^2/h \cdot m\xi \sin 2(nt - m\xi); \quad (46)$$

which is the solution used by Airy. He has given a tracing of the wave-form represented by this equation, which shows a subdivision of the wave at a sufficiently advanced station. This tracing, with a brief summary of Airy's results, is reproduced by G. H. Darwin in his article "On Tides," in the *Encyclopædia Britannica*. Airy has further carried (46) to a third approximation, which may easily be obtained from (34) and need not be reproduced here, and from this he finds there may even be a subdivision into three. All this, however, follows inevitably from the form of approximation used, that of a series of sines of multiple arcs, when due regard is not paid to the limits within which only it can be regarded as an approximation at all. In fact such an approximation will indicate a subdivision into as many waves as it contains terms; but the more terms there are taken, the further up the river must we advance before any subdivision is indicated. That great caution is necessary in applying such a series to points far up the river is further indicated by the occurrence of powers of  $\xi$  in the coefficients.

It would be equally simple to discuss the tidal phenomena produced in a river by the oceanic tides given by (33); but practically, the component tides having nearly equal periods, the discussion of the simpler tide, given by (32), suffices to give a fairly accurate account of the more complex, if we regard the range as having a slow periodic variation, the period being the interval between successive spring tides; and in fact, in referring to the effects of high and low tides, this variation was kept in view in the preceding discussion.

Dundee, December 21, 1891.

XXVI. *On the Intensity at the Focal Point of a Telescope, when the Object-glass is covered by a Diaphragm pierced with Circular Apertures.* By JAMES WALKER, M.A., Demonstrator at the Clarendon Laboratory, Oxford\*.

THE proposal recently made, to reduce the intensity of the image of a star by means of screens placed before the object-glass of a telescope, renders it of importance to determine the theoretical value of the intensity in such cases. In its general form the problem is one of considerable complexity; but when the apertures in the screen are circles, the intensity at the focal point itself can be expressed in a form from which its value can be calculated to any required degree of accuracy.

Taking the centre of the screen as origin, let the equation of one of the apertures be

$$\rho^2 - 2a\rho \cos \theta + a^2 - r^2 = 0, \quad . \quad . \quad . \quad (1)$$

where  $r$  is the radius of the circle, and  $a$  the distance of its centre from the origin; then, if we denote the aberration by  $\beta\rho^4$ , the amplitude of the displacement at the focal point may be represented by a sum of terms of the form

$$A = \int_{-\sin^{-1} r/a}^{\sin^{-1} r/a} \int_{\rho_1}^{\rho_2} e^{i\beta\rho^4} \rho \, d\rho \, d\theta, \quad . \quad . \quad . \quad (2)$$

where  $i = \sqrt{-1}$ , and  $\rho_1, \rho_2$  are the roots of (1); and the intensity at this point is obtained by multiplying this sum by the expression obtained from it by changing the sign of  $i$ .

Expanding  $e^{i\beta\rho^4}$  in a series, we at once obtain

$$\int e^{i\beta\rho^4} \rho \, d\rho = \frac{1}{2} \left\{ \rho^2 + \frac{\rho^6}{3} (i\beta) + \frac{\rho^{10}}{5} \frac{(i\beta)^2}{2} + \dots + \frac{\rho^{4n+2}}{2n+1} \cdot \frac{(i\beta)^n}{n} + \dots \right\};$$

and since

$$\rho_2^{4n+2} - \rho_1^{4n+2} = 2 \sum_{p=1}^{p=2n+1} \frac{|4n+2|}{|2p-1| |4n+3-2p|} (a \cos \theta)^{4n+3-2p} \times (r^2 - a^2 \sin^2 \theta)^{\frac{2p-1}{2}},$$

the general term of the integral (2) is

\* Communicated by the Author.



$$\begin{aligned}
 & \frac{(\iota\beta)^n}{(2n+1)} \frac{1}{[n]} \sum_{p=1}^{p=2n+1} \frac{|4n+2|}{[2p-1] |4n+3-2p|} \int_{-\sin^{-1}r/a}^{\sin^{-1}r/a} (a \cos \theta)^{4n+3-2p} \\
 & \quad \times (r^2 - a^2 \sin^2 \theta)^{\frac{2p-1}{2}} d\theta \\
 & = 2 \frac{(\iota\beta)^n}{(2n+1)} \frac{1}{[n]} \sum_{p=1}^{p=2n+1} \frac{|4n+2|}{[2p-1] |4n+3-2p|} \int_0^1 a^{4n+3} \\
 & \quad \times \left(\frac{r}{a}\right)^{2p} \left(1 - \frac{r^2}{a^2} y^2\right)^{2n+1-p} \cdot (1-y^2)^{\frac{2p-1}{2}} dy \\
 & = 2 \frac{a^{4n+3}}{2n+1} \cdot \frac{(\iota\beta)^n}{[n]} \sum_{p=1}^{p=2n+1} \frac{|4n+2|}{[2p-1] |4n+3-2p|} \\
 & \quad \times \left(\frac{r}{a}\right)^{2p} \sum_{m=0}^{m=2n+1-p} (-1)^m \left(\frac{r}{a}\right)^{2m} \frac{|2n+1-p|}{[m] |2n+1-p-m|} \cdot \frac{\Gamma\left(\frac{2m+1}{2}\right) \Gamma\left(\frac{2p+1}{2}\right)}{2\Gamma(m+p+1)}
 \end{aligned}$$

Rearranging the terms so as to collect together the coefficients of like powers of  $\frac{r}{a}$ , this expression may be written

$$\begin{aligned}
 & \frac{a^{4n+3}}{2n+1} \cdot \frac{(\iota\beta)^n}{[n]} \sum_{p=1}^{p=2n+1} \left(\frac{r}{a}\right)^{2p} \sum_{q=p-1}^{q=0} (-1)^q \frac{|4n+2|}{[2p-2q-1] |4n+3-2p+2q|} \\
 & \quad \times \frac{|2n+1-p+q|}{[q] |2n+1-p|} \cdot \frac{\Gamma\left(\frac{2q+1}{2}\right) \Gamma\left(\frac{2p-2q+1}{2}\right)}{\Gamma(p+1)} \\
 & = \sqrt{\pi} \cdot \frac{a^{4n+3}}{2n+1} \cdot \frac{(\iota\beta)^n}{[n]} \sum_{p=1}^{p=2n+1} \left(\frac{r}{a}\right)^{2p} \frac{|2n+1|}{[p] |2n+1-p|} \sum_{q=p-1}^{q=0} (-1)^q \\
 & \quad \times \frac{|2n+\frac{1}{2}|}{[p-q-1] |2n+\frac{1}{2}-p+q+1|} \cdot \frac{\Gamma\left(\frac{2q+1}{2}\right)}{[q]},
 \end{aligned}$$

using the expression  $|m+\frac{1}{2}|$  to denote

$$(m+\frac{1}{2})(m-\frac{1}{2})(m-\frac{3}{2}) \dots \frac{3}{2} \cdot \frac{1}{2}.$$

Now the expression

$$\sum_{q=p-1}^{q=0} (-1)^q \frac{|2n+\frac{1}{2}|}{[p-q-1] |2n+\frac{1}{2}-p+q+1|} \cdot \frac{\Gamma\left(\frac{2q+1}{2}\right)}{[q]}$$

is the coefficient of  $x^{p-1}$  in the product

$$(-1)^{p-1} \pi^{\frac{1}{2}} \left\{ 1 + \frac{1}{2}x + \frac{1 \cdot 3}{2 \cdot 2} \cdot \frac{x^2}{|2|} + \frac{1 \cdot 3 \cdot 5}{2 \cdot 2 \cdot 2} \cdot \frac{x^3}{|3|} + \dots \right\} \left\{ 1 - (2n + \frac{1}{2})x + (2n + \frac{1}{2})(2n - \frac{1}{2}) \frac{x^2}{|2|} - \dots \right\},$$

and this product is equal to

$$(-1)^{p-1} \cdot \pi^{\frac{1}{2}} (1-x)^{-\frac{1}{2}} (1-x)^{2n+\frac{1}{2}} = (-1)^{p-1} \cdot \pi^{\frac{1}{2}} (1-x)^{2n}.$$

Hence

$$\sum_{q=p-1}^{r=0} (-1)^q \frac{|2n + \frac{1}{2}|}{|p-q-1| |2n + \frac{1}{2} - p + q + 1|} \cdot \frac{\Gamma\left(\frac{2q+1}{2}\right)}{|q|} = \frac{|2n|}{|p-1| |2n+1-p|} \cdot \pi^{\frac{1}{2}},$$

and the general term of the integral is

$$\pi \cdot \alpha^{4n+2} \cdot \frac{(\beta)^n}{|n|} \sum_{p=1}^{p=2n+1} \frac{\{|2n\}^2}{|p| |p-1| \{|2n+1-p\}^2} \cdot \left(\frac{r}{a}\right)^{2p}.$$

We thus obtain for the amplitude of the displacement at the focal point an expression of the form

$$A = \pi \{ C_0 + C_1(\beta) + C_2(\beta)^2 + \dots \},$$

where  $C_n$  is the sum of the expressions obtained from

$$\frac{\alpha^{4n+2}}{|n|} \sum_{p=1}^{p=2n+1} \frac{\{|2n\}^2}{|p| |p-1| \{|2n+1-p\}^2} \cdot \left(\frac{r}{a}\right)^{2p}$$

by giving  $r$  and  $a$  their proper values: and the intensity is

$$I = \pi^2 \{ C_0^2 + (C_1^2 - 2C_2C_0)\beta^2 + (C_2^2 - 2C_3C_1 + 2C_4C_0)\beta^4 + \dots \}.$$

An interesting case is that in which the apertures consist of  $x$  equal circles, of which one has its centre at the middle point of the object-glass, while the centres of the remaining  $x-1$  are equidistant from this point. In this case, writing

$$r = \mu R, \quad a = \nu R,$$

where  $R$  is the radius of the full aperture of the object-glass, the value of the intensity at the focal point is

$$I = \pi^2 \cdot x^2 \mu^4 R^4 \{ D_0^2 + (D_1^2 - 2D_2D_0)\beta^2 R^2 + (D_2^2 - 2D_3D_1 + 2D_4D_0)\beta^4 R^4 + \dots \},$$

where  $D_0 = 1$ ,

$$D_n = \frac{\nu^{4n}}{[n]} \left\{ \frac{1}{2n+1} \cdot \left(\frac{\mu}{\nu}\right)^{4n} + \frac{x-1}{x} \sum_{p=1}^{p=2n} \frac{\{2n\}^2}{[p][p-1]\{2n+1-p\}^2} \cdot \left(\frac{\mu}{\nu}\right)^{2(p-1)} \right\}.$$

In the particular case of the screens supplied from the Royal Observatory, Greenwich,

$$\mu = \frac{2}{5\sqrt{7}}, \quad \nu = \frac{2}{\sqrt{7}}, \quad x = 7;$$

and hence,

$$\text{when } \beta R^4 = \frac{\pi}{4}, \quad I = \pi^2 R^4 \times 0.0256 \times 0.9811;$$

$$,, \quad \beta R^4 = \frac{\pi}{2}, \quad I = \pi^2 R^4 \times 0.0256 \times 0.9262;$$

the corresponding values of the intensity in the case of the full aperture being  $\pi^2 R^4 \times 0.9464$  and  $\pi^2 R^4 \times 0.8003$  respectively.

## XXVII. Struts and Tie-Rods with Lateral Loads.

By Professor JOHN PERRY, D.Sc., F.R.S.\*

**I** THINK that this subject has not yet been taken up scientifically; yet it is very important. The practical treatment of the whole subject of struts is in a very unsatisfactory condition; and it is mainly due to this that, of two bridges designed for the same spans and loads, by two engineers, one has sometimes more than twice the weight of the other; and in all probability the one of least weight is in some parts very much too strong, and in other parts has very little strength in excess of what is absolutely necessary.

It will be in the recollection of some of the members present that Professor Ayrton and I, in 1886, showed why experiment always gave a breaking-load for a strut which was less than that which results from Euler's theory.

A strut is a prismatic body of homogeneous material subjected to equal and opposite crushing forces at its ends. Taking its length,  $2l$ ; the least moment of inertia of its cross section about a straight line through its centre of area,  $I$ ; Young's modulus of elasticity,  $E$ ;  $f_c$  the compressive stress which the material will stand: then for a strut hinged at its ends (that is, if the resultant force at each end acts at the

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centre of the end), Euler's theory gives the breaking-load as the lesser of the two values

$$U = \frac{EI\pi^2}{4l^2}, \quad \dots \dots \dots (1)$$

$$\text{and} \quad f_c A. \quad \dots \dots \dots (2)$$

The length of strut for which these two answers are the same is

$$l = \frac{\pi k}{2} \sqrt{\frac{E}{f_c}},$$

if  $k$  is the least radius of gyration of the section about a line in the section through its centre of gravity.

Now we showed that want of homogeneity, inaccuracy of loading, and initial want of straightness in the strut all lead to a smaller load being able to break the strut, and, indeed, that an initial want of straightness (the assumption of an initial deflexion  $\alpha$  at the middle) may be taken to represent all three kinds of discrepance. We showed that for such values of  $l$  as make the two answers (1) and (2) nearly the same, a very small error  $\alpha$  produces very great discrepance—a very great diminution in the real breaking-load from Euler's breaking-load. We showed that when a strut is perfect and perfectly loaded, there is no deflexion until the breaking-load is reached; and that if a deflexion be artificially produced, the strut will straighten itself again, whereas in the imperfect strut there is a deflexion which increases at first in proportion to the load, and then more rapidly.

Such deflexions had been observed and carefully tabulated and published by Mr. Hodgkinson and Mr. Edwin Clarke, but hitherto no use had been made of them, and they had been regarded as unaccountable.

We pointed out that the error  $\alpha$  in carefully made and carefully loaded struts seems roughly to follow a rule, and consequently that without making the unwarrantable assumption which has hitherto been used to make Gordon's formula appear to be a rational one, we had a right to look upon Gordon's formula as an empirical formula, which, being of the value (2) for short struts and of the value (1) for long struts, might be taken as right for struts of any length.

Since the publication of our paper ('The Engineer,' Dec. 10th, 1886) I have been in the habit of giving to students problems on struts laterally loaded: as when a strut lies horizontally and is loaded with its own weight; or as when a strut like the coupling-rod of a locomotive, or any connecting-rod, is loaded by its own centrifugal force.

In this paper I shall first give the general solution of such problems ; and it will include the old problem of want of straightness of the strut and inaccuracy of loading.

I take as the axis of  $x$  the straight line through the centres of area of the two ends of a strut. The origin is at the point of bisection of this line. The length of strut is  $2l$ . Systems of forces act at the ends such that their resultants are two equal and opposite pushing forces  $F$  (or pulling forces  $F_1$ ) in the axis of  $x$  together with certain couples. Thus if a strut is hinged at the ends, and if the resultant forces do not act exactly through the centres of area, but at points whose distances are  $h$  (measured parallel to the plane in which bending is most likely to occur) from the centre of area, I take it that there are couples at the ends, of the amounts  $Fh$  or  $-F_1h$ . Again, if a strut is fixed at an end, I take it that there is an end couple  $-M_0$  or  $-M_1$  whose amount will be determined by given conditions of lateral loading and end push or pull. In this case  $M_0$  and  $M_1$  will include such terms as  $Fh$ . I can assume that the strut when unloaded is not quite prismatic, the ordinate of its centre line being  $y'$ . It is easy to make the treatment even more general by taking the initial shape a tortuous curve, and by considering bending as taking place in various planes ; but for nearly all practical purposes it is sufficient to deal with one plane only.

I suppose the strut to have a lateral loading such that if it were a beam *supported* merely at the ends, the bending-moment would be  $\phi(x)$ \*.

It can readily be shown that the total bending-moment at any section of a strut or tie-rod, if  $-M_0$  and  $-M_1$  are the couples at its ends, is

$$Fy + \phi(x) - \frac{1}{2}(M_0 + M_1) + x \frac{M_0 - M_1}{2l}, \dots \quad (3)$$

or

$$-F_1y + \phi(x) - \frac{1}{2}(M_0 + M_1) + x \frac{M_0 - M_1}{2l} \dots \quad (4)$$

\* If the strut is loaded uniformly laterally with a total load  $W$ ,

$$\phi(x) = \frac{1}{4}W(l^2 - x^2).$$

If the strut has a single load at the middle there is a discontinuity in the function at the middle; but we may put it

$$\phi(x) = \frac{1}{2}W(l - \sqrt{l^2 - x^2}),$$

the minus sign being taken whether  $x$  is positive or negative. There are easy graphical methods, well known to all practical engineers, for finding  $\phi(x)$  for any system of lateral loading however complicated.

The curvature being always small is  $\pm \frac{d^2y}{dx^2}$ , and we take the + or - sign according to the sign given to bending-moment, and hence we have generally for struts

$$Fy + \phi(x) - \frac{1}{2}(M_0 + M_1) + x \frac{M_0 - M_1}{2l} = -EI \left( \frac{d^2y}{dx^2} - \frac{d^2y'}{dx^2} \right),$$

or

$$\frac{d^2y}{dx^2} + \frac{F}{EI} y = \frac{d^2y'}{dx^2} - \frac{1}{EI} \phi(x) + \frac{1}{2EI} (M_0 + M_1) - \frac{x}{EI} \frac{M_0 - M_1}{2l}; \quad (5)$$

and for tie-rods we have merely to write  $-F_1$  instead of  $F$ .

I shall assume for the present that  $EI$  is constant everywhere.

Now  $\phi(x)$  can always be developed in a Fourier's series. But it will sometimes be found convenient to express it in the form

$$\phi(x) = a_0 + rx + tx^2 + a_1 \cos sx + b_1 \sin sx +$$

$$a_2 \cos 2sx + b_2 \sin 2sx + \&c. + a_4 \cos isx + b_4 \sin isx + \&c.,$$

where  $s = \frac{\pi}{2l}$ .

Terms in  $x^3$ ,  $x^4$ , &c., may easily be taken also.

We may put this symbolically as

$$\phi(x) = a_0 + rx + tx^2 + (a_i, b_i, is). \quad . \quad . \quad . \quad (6)$$

Whatever  $y'$  may be, we may express it symbolically as

$$y' = a_0 + (a_i, \beta_i, is). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence (5) may be written:—

For struts:

$$\begin{aligned} \frac{d^2y}{dx^2} + \frac{F}{EI} y = & -\frac{a_0}{EI} + \frac{M_0 + M_1}{2EI} - \frac{x}{EI} \left( r + \frac{M_0 - M_1}{2l} \right) \\ & - \frac{t}{EI} x^2 - \left( i^2 s^2 a_i + \frac{a_i}{EI}, i^2 s^2 \beta_i + \frac{b_i}{EI}, is \right); \quad . \quad . \quad (8) \end{aligned}$$

and for tie-rods we have the same equation, if  $-F_1$  be substituted for  $F$ .

Now if  $n^2$  be written instead of  $\frac{F}{EI}$  in the case of a strut and instead of  $\frac{F_1}{EI}$  in the case of a tie-rod, we have the following solutions.

For a Strut :—

$$EIy = M \cos nx + N \sin nx + A_0 + Rx + Tx^2 + (A_i, B_i, is), \quad (9)$$

where  $M$  and  $N$  are arbitrary constants,

$$A_0 = \frac{-a_0 + \frac{1}{2}(M_0 + M_1)}{n^2} + \frac{2t}{n^4}.$$

$$R = -\frac{r}{n^2} + \frac{M_1 - M_0}{2ln^2}.$$

$$T = -\frac{t}{n^2}.$$

$$A_i = -\frac{i^2 s^2 \alpha_i EI + a_i}{n^2 - i^2 s^2}.$$

$$B_i = -\frac{i^2 s^2 \beta_i EI + b_i}{n^2 - i^2 s^2}.$$

For a Tie-rod :—

$$EIy = Me^{nx} + Ne^{-nx} + A_0' + R'x + T'x^2 + (A_i', B_i', is), \quad (10)$$

where

$$n = \sqrt{\frac{F_1}{EI}},$$

where  $M$  and  $N$  are arbitrary constants,

$$A_0' = \frac{2t}{n^4} + \frac{a_0 - \frac{1}{2}(M_0 + M_1)}{n^2},$$

$$R' = \frac{r}{n^2} - \frac{M_1 - M_0}{2ln^2},$$

$$T' = \frac{t}{n^2},$$

$$A_i' = \frac{a_i + \alpha_i EI i^2 s^2}{n^2 + i^2 s^2},$$

$$B_i' = \frac{b_i + \beta_i EI i^2 s^2}{n^2 + i^2 s^2}.$$

When  $y$  is known, the greatest value of the bending-moment is known. A line through the centre of a section at right angles to the plane of bending is always called the neutral line of the section, even in cases like the present where the name is a little misleading; and if  $z_c$  and  $z_t$  are the greatest distances of points in the section from the neutral line, on the compressive and on the tensile sides respectively, and if  $\mu$  is

the greatest bending-moment, then in struts, if  $A$  is the area of cross section,

$$\frac{\mu}{I} z_c + \frac{F}{A} = f_c, \quad \dots \quad (11)$$

$$\frac{\mu}{I} z_t - \frac{F}{A} = f_t; \quad \dots \quad (12)$$

and in tie-rods,

$$\frac{\mu}{I} z_c - \frac{F_1}{A} = f_c, \quad \dots \quad (13)$$

$$\frac{\mu}{I} z_t + \frac{F_1}{A} = f_t, \quad \dots \quad (14)$$

where  $f_c$  and  $f_t$  are the maximum compressive and tensile stresses to which any part of the strut or tie-rod is subjected. In many practical cases  $z_c = z_t$ , and then  $I/z_c$  is called  $Z$ , the strength-modulus of the section.

We can therefore find the strength and stiffness of any strut of uniform section fixed or free at either or both ends when loaded laterally in any way whatever.

When, as in many practical cases, it is allowable to take an approximate value for  $\phi(x)$ , and especially when the lateral loading and initial shape are such that the strut is symmetrical about the axis of  $y$ , the work can be greatly simplified by not introducing such terms as  $r$  and  $t$ . In the symmetrical cases such terms as  $b_i$  and  $\beta_i$  are absent from the expressions, and  $M_0 = M_1$ . If the ends are not fixed,  $M_0 = M_1 = -Fh$ .

### Examples.

- I. A uniform straight strut has a lateral load  $W$  uniformly distributed. It will be found that in this case we have very nearly

$$\phi(x) = \frac{1}{4} Wl \cos \frac{\pi}{2l} x. \quad \dots \quad (15)$$

Then, if  $F$  is the resultant of the pushing forces, (8) becomes

$$\frac{d^2 y}{dx^2} + \frac{F}{EI} y = \frac{M_0}{EI} - \frac{1}{4} \frac{Wl}{EI} \cos \frac{\pi}{2l} x. \quad \dots \quad (16)$$

Solving this by the rule given above and applying the conditions that  $y=0$  when  $x=l$ , and  $\frac{dy}{dx}=0$  when  $x=0$ , it is easy



to see that the solution becomes

$$y = \frac{M_0}{F} - \frac{M_0}{F \cos l \sqrt{\frac{F}{EI}}} \cos x \sqrt{\frac{F}{EI}} + \frac{\frac{1}{4} W l}{EI \frac{\pi^2}{4l^2} - F} \cos \frac{\pi}{2l} x. \quad (17)$$

We can at once work out from this, cases in which with such a lateral loading we have any equal couples  $M_0$  applied at the ends, including the case in which the end is hinged, but the resultant push at the ends is applied with the inaccuracy  $h$ , in which case  $-M_0 = Fh$ . In case the strut is fixed at the ends

we apply the condition  $\frac{dy}{dx} = 0$ , when  $x = l$ . This gives us

$$M_0 = \frac{\pi W \sqrt{F EI}}{8(U - F)} \cot l \sqrt{\frac{F}{EI}}.$$

It is not instructive to pursue this example unless numerical values are taken for the dimensions of the strut and the loading  $W$ . If the strut is hinged at the ends and  $h = 0$ , then  $M_0 = 0$ , and

$$y = \frac{\frac{1}{4} W l}{EI \frac{\pi^2}{4l^2} - F} \cos \frac{\pi}{2l} x. \quad \dots \dots (18)$$

As this is a simple case, common in practice, I will work out the stresses.

(18) is evidently true even when  $F = 0$ . The deflexion in the middle is

$$y_1 = \frac{\frac{1}{4} W l}{EI \frac{\pi^2}{4l^2} - F}; \quad \dots \dots (19)$$

and the greatest bending-moment  $\mu$  is

$$\mu = F y_1 + \frac{1}{4} W l,$$

or

$$\mu = \frac{1}{4} W l \left( \frac{\frac{EI \pi^2}{4l^2}}{\frac{EI \pi^2}{4l^2} - F} \right). \quad \dots \dots (20)$$

If  $W = 0$  and if  $\mu$  has any value whatever, the denominator must be 0. Putting it equal to 0, we have Euler's law for the strength of struts which are so long that they bend before

breaking. If Euler's value of  $F$  be called  $U$ ,

$$U = \frac{EI\pi^2}{4l^2}. \quad \dots \quad (21)$$

Using this as a symbol, (20) becomes

$$\mu = \frac{1}{4} Wl \frac{U}{U - F}; \quad \dots \quad (22)$$

and we can at once apply (11) and (12) to find the greatest compressive and tensile stresses in the strut. Then, writing  $\frac{U}{A}$  as  $\beta$ , and  $\frac{F}{A}$  as  $\omega$ , we see that if  $f$  is the compressive stress which the material will bear,

$$\left(1 - \frac{\omega}{f}\right) \left(1 - \frac{\omega}{\beta}\right) = \frac{Wl}{4fZ}. \quad \dots \quad (23)$$

From this, if we are given the dimensions of the strut and  $f$  and  $W$ , it is easy to calculate  $\omega$ . The solution of the quadratic is

$$2\omega = f + \beta - \sqrt{(f + \beta)^2 + \left(\frac{Wl}{Z} - 4f\right)\beta}, \quad \dots \quad (24)$$

the *minus* sign being taken because  $\omega$  is evidently less than  $f$  and less than  $\beta$ .

*Coupling-Rods.*—Starting from this result, my students have for several years worked out the relative breadths and thicknesses of the sections of coupling-rods and connecting-rods of engines, which are struts whose lateral loads are due mainly to centrifugal force.

Every point in a coupling-rod describes a circle of radius  $r$  inches. If the section is, say, rectangular (an elliptic section is just as easy to deal with) of dimensions  $d$  in the plane of motion and  $b$  at right angles to the plane of motion; taking the whole mass as  $2lb d \times .28$  divided by  $32.2$ ; the centrifugal force

$$W = \frac{lbdrn^2}{62940} \text{ lbs. wt.}$$

if the rod makes  $n$  revolutions per minute.

In one direction a coupling-rod is a strut hinged at the ends, and the thrust per square inch that it can receive, assuming that it is properly made, is to be the same as the thrust which it will stand in the other direction. In the first direction it has lateral loading due to centrifugal force.

Now it might be supposed that in the second direction the strut is as if fixed at the ends ; but the pins are very short, and the resultant load is certainly not applied axially, and it is safer to assume that in this direction also the strut is as if hinged at the ends. I assume this, although perhaps from the possibility of accidental untrue loading we ought to go further in this safe direction and assume that the strength of the strut is less. Assuming it hinged also in the second direction, however, the thrust per square inch which it can receive is  $EI_1 \frac{\pi^2}{4l^2} / bd$ , and in this case  $I_1 = \frac{db^3}{12}$  ; so that, if  $E = 3 \times 10^7$ ,

$$\omega = 6.17 \frac{b^2}{l^2} \times 10^6.$$

This is the value to use in formula (23).

Taking  $f$  for the steel used as 20,000 lb. per square inch, being the proof stress which the material will stand for an infinite number of reversals of stress, we find for equal strength in the two directions, applying (23), that

$$8.4 \times 10^8 \left(1 - 308 \frac{b^2}{l^2}\right) \left(1 - \frac{b^2}{d^2}\right) = n^2 l^2 r / d.$$

Thus, for example, if  $b=1$ , and  $l=30$ , and  $r=12$ , we have the following tables:—

If  $b=1$ .

$d$ .	$n$ .
1	0
1.5	205
2	277
2.5	327
3	368
4	437
6	545

If  $b=1.5$ .

$d$ .	$n$ .
1.5	0
2	125
2.5	170
3	202
4	249
6	318
10	440

To illustrate these results. On a certain locomotive engine the coupling-rods are 68 inches long or  $l=34''$ ,  $d=3\frac{1}{2}$ ,  $b=1\frac{3}{8}$ ,  $r=12$ .

Now it will be found that this rod is equally strong in the two directions if  $n=298$  revolutions per minute. The limit of speed which has practically been settled for the engine by the breaking of similar coupling-rods is 258 revolutions per minute.

Without trying to make a rod equally strong to resist bending in the two directions, it is interesting to consider the  $F$  or rather  $\omega$  which a coupling-rod will stand when revolving at  $n$  revolutions per minute.

Using (24) and taking

$$E = 3 \times 10^7, \quad \frac{Wl}{Z} = \frac{l^2 r n^2}{10490d},$$

$\beta = 6.17 \times 10^6 \frac{d^3}{l^2}$ , so that  $\omega$  does not depend upon  $b$ .

If  $l=30$  and  $r=12$ , and  $f=20,000$ , we find for various values of  $d$  and  $n$  the following values of  $\omega$  :—

Values of $n$ .	$\omega$ if $d=2$ .	$\omega$ if $d=3$ .	$\omega$ if $d=4$ .
0	20000	20000	20000
100	18720	18810	19090
200	11760	15455	16930
300	5505	10690	13400
350	2615	7880	11150
394	0	.....	.....
400	.....	5070	8800
450	.....	2045	6150
483	.....	0	.....
500	.....	.....	3400
557	.....	.....	0

Taking as before  $l=30$  and  $r=12$ , but now  $f=10,000$ , we find :—

Values of $n$ .	$\omega$ if $d=2$ .	$\omega$ if $d=3$ .	$\omega$ if $d=4$ .
0	10000	10000	10000
100	8166	8995	9500
200	3976	6185	8450
250	1490	4240	.....
279	0	.....	.....
300	.....	2010	4200
340	.....	0	.....
350	.....	.....	2050
394	.....	.....	0

It is quite easy to make similar calculations on sections of **I** shape. Rods of this section may be made equally strong to resist bending in the two directions, at much higher speeds than are possible in the case of the rectangular

section. The elliptic section is not so good as the rectangular, and the I section is better than either.

II. A uniform straight tie-rod has a lateral total load  $W$  uniformly distributed. The resultant of pulling forces at the ends is  $F_1$  and passes exactly through the centres of the ends ; (8) becomes

$$\frac{d^2y}{dx^2} - \frac{F_1}{EI}y = + \frac{M_0}{EI} - \frac{\frac{1}{2}Wl}{EI} \cos \frac{\pi}{2l}x. \quad (25)$$

Using  $n^2$  for  $\frac{F_1}{EI}$ ,

$$y = Me^{nx} + Ne^{-nx} - \frac{M_0}{n^2EI} + \frac{\frac{1}{2}Wl \cos \frac{\pi}{2l}x}{EI\left(n^2 + \frac{\pi^2}{4l^2}\right)}. \quad (26)$$

Applying the conditions  $y=0$  when  $x=l$ , and  $\frac{dy}{dx}=0$  when  $x=0$ , we find

$$y = \frac{M_0}{EI n^2} \left\{ \frac{e^{nx} + e^{-nx}}{e^{nl} + e^{-nl}} - 1 \right\} + \frac{\frac{1}{2}Wl \cos \frac{\pi}{2l}x}{EI\left(n^2 + \frac{\pi^2}{4l^2}\right)}. \quad (27)$$

If we suppose that no couples are applied at the ends, or  $M_0=0$ ,

$$y = \frac{\frac{1}{2}Wl \cos \frac{\pi}{2l}x}{F_1 + \frac{\pi^2}{4l^2}EI}. \quad (28)$$

This is identical with (18) if  $F_1 = -F$ . So that in this simple case we can use the same expression for the shape, whether the bar is a strut or a tie-rod.

In the case of a strut,

$$\frac{\frac{1}{2}Wl}{Z} \frac{U}{U-F} + \frac{F}{A} = f_s, \quad (29)$$

$$\frac{\frac{1}{2}Wl}{Z} \frac{U}{U-F} - \frac{F}{A} = f_t, \quad (30)$$

and by taking  $F$  in the expressions negative, we find  $f_s$  and  $f_t$  in a tie-rod.

A numerical example will illustrate these formulæ. I will take a round rod of mild steel lying in a horizontal position, so that it is loaded laterally by its own weight, dimensions being in inches. If  $d$  is its diameter, the weight of 1 cubic inch of material is 0.28 lb. and  $E = 3 \times 10^7$ ,

$$I = \frac{\pi d^4}{64} \quad \text{and} \quad Z = \frac{\pi d^3}{32}, \quad U = 3.6 \times 10^6 \frac{d^4}{l^2},$$

$$f_c \text{ or } f_t = \frac{4.03 \times 10^6 d^3}{3.6 \times 10^6 \frac{d^4}{l^2} - F} \pm \frac{F}{\frac{\pi}{4} d^2};$$

the *plus* sign being taken in calculating  $f_c$  and the *minus* in calculating  $f_t$ . Also

$$y_1 = \frac{.11 d^2 l^2}{3.6 \times 10^6 \frac{d^4}{l^2} - F}.$$

Take  $d = 1$  inch,  $l = 60$  inches,

$$f_c \text{ or } f_t = \frac{4.03 \times 10^6}{1000 - F} \pm 1.273 F \quad \text{and} \quad y_1 = \frac{396}{1000 - F}.$$

From this I have calculated the following table. The negative values of  $F$  indicate that instead of a strut we have a tie.

F.	$f_c$ .	$f_t$ .	$y_1$ .
1000	$\infty$	$\infty$	$\infty$
900	41446	39154	3.96
800	21168	19182	1.98
700	14324	12542	1.32
500	8697	7423	0.792
300	6648	4866	0.566
100	4605	4351	0.440
0	4030	4030	0.396
- 100	3537	3791	0.360
- 300	2718	3482	0.305
- 500	2031	3323	0.264
- 700	1479	3261	0.233
- 900	975	3267	0.208
- 1200	304	3360	0.180
- 1348	0	3432	0.169

We see, then, that a comparatively small thrust  $F$  produces excessive stress in the strut and great deflexion  $y_1$ .

We see also that a tensile force  $F_1$  of 900 lb. halves the

deflexion of the unpulled beam, and not only reduces the compressive stress to less than a quarter of its old amount, but it has also reduced the tensile stress by nearly 20 per cent. And a tensile load  $F_1$  of 1348 lb. completely destroys all compressive stress in the strut, whilst reducing the greatest tensile stress of the unpulled strut by 15 per cent.

In fact when a beam is very long, pulling out its ends may reduce the compressive stress in it to nothing, whilst also reducing the tensile stress. A longer or smaller beam than that which I have taken will illustrate this matter even better.

The tension  $F_1$  which will make  $f_i$  a minimum is

$$F_1 = \sqrt{\left(\frac{AWl}{4Z} U\right)} - U,$$

and when  $\frac{AWl}{4Z}$  is so small as  $U$  then the unpulled beam itself has the minimum tensile stress.

If  $\frac{AWl}{4Z}$  is less than  $U$  it requires a pushing force  $F$  to give the minimum tensile stress.

In all cases there is, of course, a pulling force  $F_1$  which will cause the beam to have no compressive stress in it. In some cases there is a pushing force  $F$  which will cause the beam to have no tensile stress in it, but this can only be the case when

$$U \text{ is not less than } \frac{WlA}{Z}.$$

In this case, a beam to carry lateral load may be built up of separate blocks of material which have just sufficient friction to prevent slipping due to shearing forces at the joints. It is a case which may be treated graphically by Professor Fuller's Method, as the change of shape is small.

It will be seen from the above simple example that very instructive numerical problems may be given. Thus if, instead of the lateral loading, we have merely couples,  $-M_0$  or  $m$ , applied to the ends of a strut, we use  $W = 0$  in (17).

When  $x=0$  we have the greatest value of  $y_1$ , or

$$y_1 = \frac{m}{F} \left\{ \frac{1}{\cos l \sqrt{\frac{F}{EI}}} - 1 \right\}.$$

Also  $Fy_1 + m = \mu$  the greatest bending-moment in the strut,

or

$$\mu = \frac{m}{\cos l \sqrt{\frac{F}{EI}}}$$

$$f_c = \frac{m}{Z \cos l \sqrt{\frac{F}{EI}}} + \frac{F}{A},$$

$$f_t = \frac{m}{Z \cos l \sqrt{\frac{F}{EI}}} - \frac{F}{A}.$$

Taking for numerical example a round bar of steel as before, and taking  $d=1$  inch,  $l=48$  inches, and writing the angle in degrees to simplify calculation, we have

$$f_c \text{ or } f_t = \frac{10.2m}{\cos 2.267 \sqrt{F}} \pm 1.273F,$$

$$y_1 = \frac{m}{F} \left\{ \frac{1}{\cos 2.267 \sqrt{F}} - 1 \right\}.$$

If  $F=0$ ,  $f_c$  or  $f_t=10.2 m$ ,  $y_1 = \frac{m l^2}{2EI}$  or  $7.821 \times 10^{-4} m$ ,

Euler's strength or  $U$  for this strut is 1577 lb. It is evidently obtainable by putting the quantity inside the bracket equal to infinity.

First take  $F=1500$  lb. Then

$$y_1 = \frac{m}{60}, \quad 2.267 \sqrt{F} = 87.80,$$

$$f_c \text{ or } f_t = 266m \pm 1910.$$

$m.$	$f_c.$	$f_t.$	$y_1.$	$f_c \text{ or } f_t,$ if $F=0.$
0	1910	-1910	0	0
1	2176	-1644	.0167	10.2
2	2442	-1378	.0333	20.4
3	2708	-1112	.0500	30.6
5	3240	-580	.0833	51.0
7.18	3820	0	.1197	73.2
10	4570	750	.1667	102
20	7230	3410	.3333	204
80	28190	19370	1.333	816

So that an endlong load only sufficient by itself to produce



a stress of 1910 lb. per sq. inch and a bending-moment which by itself would only produce a stress of 816 lb. per sq. inch, if both act together, produce a stress of 23190 lb. per sq. inch. In fact, the stress due to  $m$  alone is intensified more than 26 times.

Similarly with an endlong thrust of 1400 lb. the stress due to the lateral bending-moment  $m$  is intensified 11.04 times. With an endlong thrust of 1000 lb. the stress due to  $m$  is intensified 3.185 times. With an endlong thrust of 500 lb. the stress due to  $m$  is intensified 1.58 times.

It is obvious that in any strut the stress due to  $m$ , a lateral bending-moment, is more and more intensified as  $F$  approaches Euler's load  $U$ . And if  $m$  is due to an inaccuracy of loading,  $h$ , the effect becomes four times as noticeable in struts of half the length.

From the above example one sees that it was quite possible for a strong man like Samson to exert a sufficient lateral force to produce fracture in the columns of the temple at Gaza.

Professor Fuller's graphical method of dealing with a metal arched rib is not applicable to struts unless we assume  $Fy=0$ , and this is of course a very wrong assumption. For the same reason, the graphical method cannot be applied to very flat arches, because it assumes that we know the shape of the loaded arch. If Professor Fuller's method were applicable, we could at once deal graphically with a strut of varying section. This case does not usually need to be solved in practice, but if it must be solved the following method will do.

1st. Assume that  $EI$  is constant and of its average value, and obtain the shape of the strut as in (10).

2nd. Use this value of  $y$  in the term  $\frac{F}{EI}y$  of (8); and use the proper value of  $I$  expressed as a function of  $x$ , and then by mere integration of (8) find the more correct value of  $y$ .

By repeating this process we can obtain  $y$  more and more accurately.

### Problem.

When a strut is loaded laterally (say uniformly), say that it is hinged at the ends; it is possible by applying the endlong thrust  $F$  untruly, that is making the resultant thrust pass through a point  $h$  inches from the centre of each end, to give such a value to  $h$  as will enable the strut to withstand a maximum load  $F$ . In this case it is obvious that the greatest

compressive stresses are :—

$$\text{at the ends, } f = F \left( \frac{h}{Z} + \frac{1}{A} \right);$$

$$\text{at the middle, } f = \frac{F}{A} + \frac{\frac{1}{2} W l}{Z} \frac{U}{U - F} - \frac{F h}{Z \cos l \sqrt{\frac{F}{EI}}}.$$

The problem to find for a given strut and given maximum stress  $f$  the value of  $h$  which will cause  $F$  to be a maximum is easily worked out if a numerical example be taken.

It is obvious from this and from other examples that may be taken, that whether a strut is loaded laterally or is imperfectly straight or has other faults which would cause it to break with a load  $F$  smaller than  $U$  and  $fA$ , it is always possible to adjust the loading so that  $F$  may be increased. Thus if a strut is being tested and if for small loads we find that it deflects, the load ought to be readjusted in such a way that its application produces the minimum deflexion; and now if the load is increased we shall find that the strut breaks with a much greater load than if we had not adjusted the method of its application. This adjustment of the method of loading ought to be applied also in the building of structures.

It will be seen that I have merely touched on a few of the many very interesting problems on structures to which the general treatment (3) to (30) may be applied. The lateral load required to prevent a straight strut from bending and to cause its breaking-thrust to be  $fA$  is evidently small. We can assume, however, an initial want of straightness or an accidental deflexion, and so find how very slight need be the diagonal bracing in the large struts used in bridge-building.

I have to thank Messrs. Field and Clinton, of the Finsbury College, for checking the mathematical work in this paper.

### XXVIII. *The Hypothetical Tetrachloride of Manganese.*

By SPENCER UMFREVILLE PICKERING, F.R.S.\*

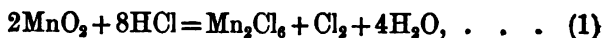
**I**N a paper read before the Chemical Society in April, 1890, Mr. H. M. Vernon adduced some evidence which apparently he considered to be adverse to my conclusion that the higher chloride of manganese was  $Mn_2Cl_6$ , and not  $MnCl_4$ ; and at the same time he attempted to demolish the evidence on which my original conclusions were based, although he did not in any way question the validity of the objections which

\* Communicated by the Author.

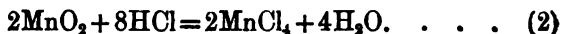
I raised against those arguments which had previously been used to support this formula (see Chem. Soc. Trans. 1878, p. 409). Mr. Vernon's paper has recently appeared *in extenso* in this Magazine (vol. xxxi. p. 439).

The evidence adduced by me (Chem. Soc. Trans. 1879, p. 654) in favour of the formula  $\text{Mn}_2\text{Cl}_6$  was :—

1. That the dissolution of manganese dioxide in hydrochloric acid results in the (almost) immediate liberation of two atoms of free chlorine for every two of loosely combined chlorine present in the higher chloride formed, according to the equation



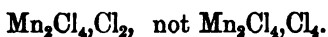
instead of resulting in the liberation of no free chlorine, as might be the case if the tetrachloride were formed:



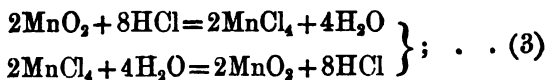
This fact was established by finding that of the total available (*i.e.* free + loosely combined), chlorine present, one half might be removed from the liquid very quickly (in about half an hour) by a rapid current of air, whereas many days are required to remove the remaining half in the same way, this second half being evidently present not as free chlorine, but as the result of the gradual decomposition of the higher chloride:



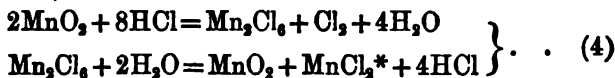
2. That although a lowering of temperature increases the stability of the higher chloride, the amount formed tends towards a limit which no further lowering of temperature will modify, this limit being that at which every two atoms of manganese present as the higher chloride retain 2 and not 4 atoms of loosely combined chlorine,



The amount of loosely combined chlorine was estimated by decomposing the higher chloride with excess of water: if  $\text{MnCl}_4$  were formed, the whole of the dioxide taken might be recovered,



whereas if  $\text{Mn}_2\text{Cl}_6$  were formed, only 50 per cent. of it could be recovered,



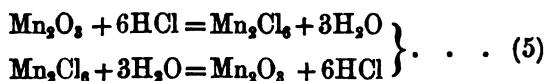
The maximum amount recovered was 47 per cent. at  $-20^\circ$ , the results plotted against temperature being represented by a curve which had at this point become nearly parallel to the axis.

3. That the amount of higher chloride formed may be very materially increased by adding a small quantity of manganous chloride to the acid used to dissolve the dioxide; this might be the case if the higher chloride were  $\text{Mn}_2\text{Cl}_6$ ,



but could not be the case if the higher chloride were  $\text{MnCl}_4$ . One molecular proportion of the manganous chloride increased the amount of higher chloride from 45 to 80 per cent., and there was a very marked change of curvature at this point, it requiring another 4 molecules of the manganous chloride to increase the amount of higher chloride by another 15 per cent.

4. That the sesquioxide will dissolve in hydrochloric acid with practically no evolution of free chlorine, and that nearly the whole of the available oxygen which the former contains may be recovered when the action is reversed by decomposing the solution with excess of water.



With one exception, which may be easily explained, Mr. Vernon's experiments add confirmation to all these results. I proceed to take them *seriatim*.

1. *The first half of the available chlorine is evolved much more rapidly than the second half.* On p. 476 of Mr. Vernon's paper we find several determinations at comparatively high temperatures. In one of them, for instance (that at  $75^\circ$ ), "more than half the gas comes off in the first minute," the other half requiring 30 minutes for its evolution. At lower temperatures ( $18^\circ$ ), the only experiment which was made to ascertain whether the rates at which the two halves of the chlorine were evolved were different (Experiment I. p. 473) showed that a current of air carried off 45.9 per cent. in the first hour, and only 24.5 per cent. more in the next three

\* Or a corresponding amount of  $\text{MnO}$ .

hours. Thus my above-stated conclusion is confirmed, nor does Mr. Vernon attempt to investigate the question further by obtaining sufficient details for determining whether the rates of evolution at different points may be represented by a uniform curve or not: it is only in the experiment last referred to that he gives any details at all, and those given here are altogether insufficient for the purpose—only 3 values for the rates.

Experiments II. and III., pp. 473, 474, were determinations of the amount of chlorine carried away in two hours by a current of air when the liquid was kept at  $-14^{\circ}$ ,  $-6^{\circ}$ , and  $-26^{\circ}$  respectively. At the lowest of these temperatures 1.8 per cent. only of the available chlorine was removed, and the smallness of this amount shows "conclusively," according to Mr. Vernon, "that when manganese dioxide dissolves in hydrochloric acid, manganese tetrachloride and no free chlorine are originally formed." As this conclusion, however, is directly opposed to that which Mr. Vernon is obliged to draw from some subsequent experiments, there must be some error either in the present or in these subsequent experiments. The present ones are, no doubt, at fault. We learn from Mr. Vernon that even at the highest of these three temperatures,  $-6^{\circ}$ , and after the current of air had been bubbled through the liquid for two hours, a considerable portion of the manganese dioxide was still undissolved, and had to be separated by filtration through a filter-paper and estimated; presumably this was done in the experiment at  $-26^{\circ}$  also. Now Mr. Vernon's original paper, when read before the Chemical Society, contained an account of an experiment precisely similar to the one at  $-26^{\circ}$  here given, except that in it the precaution of estimating the undissolved dioxide was not taken, and the chlorine removed was then found to be only 0.35 per cent. of the total which might have been obtained, whereas here it is 1.8 per cent. of the total obtainable from that portion which was dissolved, so that less than  $\frac{1}{5}$  of the dioxide taken had been dissolved: presumably again (for Mr. Vernon is very chary of details) about 3 grams of an oxide having the composition given on p. 473 were taken, and if this be so, a simple calculation will show that the observed 1.8 per cent. of chlorine would become converted into 50 per cent. (the value which we ought to get if the higher chloride were  $Mn_2Cl_6$ , see equation 4) if only .027 gram of the dioxide had got into the filtrate accidentally. The filtration of a strongly acid liquid through filter-paper is often not very satisfactory, and this small amount might easily have passed through unsuspected in the dark liquid, but a still

simpler explanation is that it had dissolved *during* the filtration and after the estimation of the evolved chlorine, especially as no precautions whatever were taken to keep the liquid at  $-26^{\circ}$  while being filtered, and as (according to Mr. Vernon himself) the solubility of the dioxide increases rapidly with a rise of temperature. Some error of unknown magnitude must, at any rate, have been introduced in this way, and would render the results entirely untrustworthy, yet on these results, although opposed to his subsequent experiments, Mr. Vernon's sole argument against the higher chloride being  $\text{Mn}_2\text{Cl}_6$  depends.

2. *The greatest amount of available oxygen obtained by decomposing the higher chloride by water is 50 per cent. of that present in the dioxide taken* (see equation 4). If the dioxide contains any protoxide the amount recoverable will be increased, one gram molecule increasing it to 100 per cent. (equation 5). The sample used by me contained a little monoxide, for the presence of which due allowance was made (although Mr. Vernon concludes otherwise); and Mr. Vernon, therefore, made some experiments "to see if it were not possible to recover more than this (50) percentage when pure dioxide was used." Unfortunately, however, he has forgotten to say anything about the results of these experiments, and, more unfortunately still, in those experiments with impure oxides which he does quote he has forgotten to make any allowance for the impurity (protoxide) which they contained. Making this correction for him, his results are as follows:—

I.		II.		III.
at $5^{\circ}$ .	at $-9^{\circ}$ .	at $18^{\circ}$ .		at $18^{\circ}$ .
51.4	51.0	45.4	46.1	47.6 per cent. of the dioxide recovered.

The numbers scarcely warrant the conclusion that "instead of the amount of dioxide recovered being always slightly below fifty per cent. it is always slightly above it." It is only above it in one case; and then by such a small amount that it is entirely insignificant in experiments depending on the results of two rather difficult analyses, especially as Mr. Vernon gives the results of but one analysis in the whole of his paper, affording us, therefore, no data from which to judge of the magnitude of his experimental error. It is interesting to note that Mr. Vernon's results in experiment I. confirm my own conclusion that a reduction of temperature below about  $6^{\circ}$  causes no appreciable increase in the dioxide recovered.

Mr. Vernon having concluded that a little over, but not much over, 50 per cent. may be recovered, naturally finds

some difficulty in reconciling this with the supposed results of his previous experiments, which, he thought, showed that "the tetrachloride and no free chlorine are originally formed," and that at low temperatures the tetrachloride is scarcely decomposed after two hours, in which case, of course, 100 per cent. of the dioxide taken would be recoverable. His expedient for reconciling these results may be ingenious, but will, I fear, scarcely commend itself to scientific men. It is that "at no temperature will the number of molecules of  $\text{MnCl}_4$  be much greater than half" of the maximum possible, the other half being split up into manganous chloride and atoms of chlorine, and that these atoms of chlorine at ordinary temperatures unite to form molecules and are liberated as such, whereas at low temperatures they are sufficiently accommodating as to "come less often into the positions necessary for them in order that they may unite together," and hence they remain in the liquid as free atoms! Mr. Vernon does not see that, even if such a specious hypothesis could be accepted, it entirely cuts the ground from under his feet. His argument that the higher chloride is  $\text{MnCl}_4$  depends on all the chlorine liberated by the dioxide remaining combined with the manganese. If he invents a method for retaining some of it in the liquid without its being combined with the manganese, what proof has he of any particular formula at all for the higher chloride?

3. *That the amount of higher chloride formed is largely increased by dissolving the dioxide in the presence of a molecular proportion of a manganous chloride.* The amount which I found, as mentioned above, was nearly doubled by the addition of one molecular proportion, the rate of increase being represented by a line "which differed little from a straight line" up to about this point, after which it diminished very rapidly. Mr. Vernon concludes, as in the former case, that I did not make allowance for the protoxide contained in the dioxide taken, and that therefore the change of curvature did not occur when 1, but when 1.132 molecules of manganous chloride had been added. Why he should draw such a conclusion it is impossible to say\*, for I stated on p. 657 that "the 9 per cent. of protoxide which the sample of oxide used by me contained was allowed for in calculating out the results wherever necessary;" and I find, on reference to my laboratory note-book, that this allowance was duly made in the present case. Even had it not been, this would not have weakened my argument, for with such determina-

\* Unless it is that a point is inserted in my diagram at the zero-point, which is obviously incorrect.

tions it was not possible to locate the point at which the change of curvature occurred within about .1 molecule.

Referring to the straightness of my curve up to the addition of one molecule of manganous chloride, Mr. Vernon remarks that "it can be shown mathematically that the form of the curve up to the addition of one molecule of  $\text{MnCl}_2$  will not be a straight line." Had Mr. Vernon but favoured us with the mathematics of this very complicated reaction, he would have conferred a benefit on science and put its ablest representatives into the shade.

The increase in the amount of the higher chloride Mr. Vernon attempts to explain by the latter being a dissociation-product of  $\text{MnCl}_4$ ; and, after reproducing an elementary text-book *exposé* of how the presence of excess of dissociation-products will reduce the amount of substance dissociated, concludes that "if, therefore, a large excess of  $\text{MnCl}_2$  is present" there will be "much less decomposition." But he forgets that my results show that it does not require a *large excess*, but only one molecular proportion of manganous chloride to increase the higher chloride present to double its former amount, and that a large excess in addition to this has but a small additional effect on the results. In order, however, to remove the least chance of his explanation being accepted, Mr. Vernon proceeds to show by experiment that the presence of dissociation-products—or at any rate of the other dissociation-product, the chlorine—has *no* appreciable effect on increasing the amount of the higher chloride.

4. *Manganese sesquioxide dissolves in hydrochloric acid without the liberation of any free chlorine, and nearly the whole of the available oxygen in it can be removed on decomposing the solution with water.* Mr. Vernon confirms this, p. 483.

Thus it will be seen that the only tittle of the evidence adduced by Mr. Vernon which might at first sight appear to militate against my conclusion as to the formula of the higher chloride is based on experiments which are obviously faulty, and leads to results diametrically opposed to even his own experimental results, while in every other particular he simply confirms my observations.

I have refrained from criticising all the details of Mr. Vernon's paper; but I venture to think that those who study these details will certainly arrive at no other conclusion than that to which a study of his main arguments leads, namely, that whatever be the real nature of the higher chloride of manganese, Mr. Vernon's results have thrown no fresh light upon the subject, nor have they in any way invalidated the existing evidence for considering it to be the sesquichloride,

July, 1891.



XXIX. *The Kinetic Theory of the Dissipation of Energy.*

By Sir WILLIAM THOMSON\*.

**I**N abstract dynamics the instantaneous reversal of the motion of every moving particle of a system causes the system to move backwards, each particle of it along its old path, and at the same speed as before, when again in the same position. That is to say, in mathematical language, any solution remains a solution when  $t$  is changed into  $-t$ . In physical dynamics this simple and perfect reversibility fails, on account of forces depending on friction of solids; imperfect fluidity of fluids; imperfect elasticity of solids; inequalities of temperature, and consequent conduction of heat produced by stresses in solids and fluids; imperfect magnetic retentiveness; residual electric polarization of dielectrics; generation of heat by electric currents induced by motion; diffusion of fluids, solution of solids in fluids, and other chemical changes; and absorption of radiant heat and light. Consideration of these agencies in connexion with the all-pervading law of the conservation of energy proved for them by Joule, led me twenty-three years ago to the theory of the dissipation of energy, which I communicated first to the Royal Society of Edinburgh in 1852, in a paper entitled "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy."

The essence of Joule's discovery is the subjection of physical phenomena to dynamical law. If, then, the motion of every particle of matter in the universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after. The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water; the thermal motions would reconcentrate their energy, and throw the mass up the fall in drops re-forming into a close column of ascending water. Heat which had been generated by the friction of solids and dissipated by conduction, and radiation with absorption, would come again to the place of contact, and throw the moving body back against the force to which it had previously yielded. Boulders would recover from the mud the materials required to rebuild them into their previous jagged forms, and would become reunited to the mountain peak from which they had formerly broken away. And if also the materialistic hypothesis of life were true, living creatures would grow backwards, with conscious knowledge of the future, but no memory of the past, and would become again unborn. But the real phenomena of life infinitely

\* Communicated by the Author; having been originally published in the Proceedings of the Royal Society of Edinburgh for February, 1874.

transcend human science ; and speculation regarding consequences of their imagined reversal is utterly unprofitable. Far otherwise, however, is it in respect to the reversal of the motions of matter uninfluenced by life, a very elementary consideration of which leads to the full explanation of the theory of dissipation of energy.

To take one of the simplest cases of the dissipation of energy, the conduction of heat through a solid—consider a bar of metal warmer at one end than the other, and left to itself. To avoid all needless complication of taking loss or gain of heat into account, imagine the bar to be varnished with a substance impermeable to heat. For the sake of definiteness, imagine the bar to be first given with one-half of it at one uniform temperature, and the other half of it at another uniform temperature. Instantly a diffusing of heat commences, and the distribution of temperature becomes continuously less and less unequal, tending to perfect uniformity, but never in any finite time attaining perfectly to this ultimate condition. This process of diffusion could be perfectly prevented by an army of Maxwell's "intelligent demons,"\* stationed at the surface, or interface as we may call it with Professor James Thomson, separating the hot from the cold part of the bar. To see precisely how this is to be done, consider rather a gas than a solid, because we have much knowledge regarding the molecular motions of a gas, and little or no knowledge of the molecular motions of a solid. Take a jar with the lower half occupied by cold air or gas, and the upper half occupied with air or gas of the same kind, but at a higher temperature ; and let the mouth of the jar be closed by an air-tight lid. If the containing vessel were perfectly impermeable to heat, the diffusion of heat would follow the same law in the gas as in the solid, though in the gas the diffusion of heat takes place chiefly by the diffusion of molecules, each taking its energy with it, and only to a small proportion of its whole amount by the interchange of energy between molecule and molecule ; whereas in the solid there is little or no diffusion of substance, and the diffusion of heat takes place entirely, or almost entirely, through the communication of energy from one molecule to another. Fourier's exquisite mathematical analysis expresses perfectly the statistics of the process of diffusion in each case, whether it be "conduction of heat," as Fourier and his followers have called it, or the diffusion of substance in fluid masses (gaseous or

\* The definition of a demon, according to the use of this word by Maxwell, is an intelligent being endowed with free-will and fine enough tactile and perceptive organization to give him the faculty of observing and influencing individual molecules of matter.

liquid), which Fick showed to be subject to Fourier's formulas. Now, suppose the weapon of the ideal army to be a club, or, as it were, a molecular cricket bat; and suppose, for convenience, the mass of each demon with his weapon to be several times greater than that of a molecule. Every time he strikes a molecule he is to send it away with the same energy as it had immediately before. Each demon is to keep as nearly as possible to a certain station, making only such excursions from it as the execution of his orders requires. He is to experience no forces except such as result from collisions with molecules, and mutual forces between parts of his own mass, including his weapon. Thus his voluntary movements cannot influence the position of his centre of gravity, otherwise than by producing collision with molecules.

The whole interface between hot and cold is to be divided into small areas, each allotted to a single demon. The duty of each demon is to guard his allotment, turning molecules back, or allowing them to pass through from either side, according to certain definite orders. First, let the orders be to allow no molecules to pass from either side. The effect will be the same as if the interface were stopped by a barrier impermeable to matter and to heat. The pressure of the gas being by hypothesis equal in the hot and cold parts, the resultant momentum taken by each demon from any considerable number of molecules will be zero; and therefore he may so time his strokes that he shall never move to any considerable distance from his station. Now, instead of stopping and turning all the molecules from crossing his allotted area, let each demon permit a hundred molecules chosen arbitrarily to cross it from the hot side; and the same number of molecules, chosen so as to have the same entire amount of energy and the same resultant momentum, to cross the other way from the cold side. Let this be done over and over again within certain small equal consecutive intervals of time, with care that if the specified balance of energy and momentum is not exactly fulfilled in respect to each successive hundred molecules crossing each way, the error will be carried forward, and as nearly as may be corrected, in respect to the next hundred. Thus, a certain perfectly regular diffusion of the gas both ways across the interface goes on, while the original different temperatures on the two sides of the interface are maintained without change.

Suppose, now, that in the original condition the temperature and pressure of the gas are each equal throughout the vessel, and let it be required to disequalize the temperature, but to leave the pressure the same in any two portions A and B of the whole space. Station the army on the interface as

previously described. Let the orders now be that each demon is to stop all molecules from crossing his area in either direction except 100 coming from A, arbitrarily chosen to be let pass into B, and a greater number, having among them less energy but equal momentum, to cross from B to A. Let this be repeated over and over again. The temperature in A will be continually diminished and the number of molecules in it continually increased, until there are not in B enough of molecules with small enough velocities to fulfil the condition with reference to permission to pass from B to A. If after that no molecule be allowed to pass the interface in either direction, the final condition will be very great condensation and very low temperature in A; rarefaction and very high temperature in B; and equal pressures in A and B. The process of disequalization of temperature and density might be stopped at any time by changing the orders to those previously specified, and so permitting a certain degree of diffusion each way across the interface while maintaining a certain uniform difference of temperatures with equality of pressure on the two sides.

If no selective influence, such as that of the ideal "demon," guides individual molecules, the average result of their free motions and collisions must be to equalize the distribution of energy among them in the gross; and after a sufficiently long time, from the supposed initial arrangement, the difference of energy in any two equal volumes, each containing a very great number of molecules, must bear a very small proportion to the whole amount in either; or, more strictly speaking, the probability of the difference of energy exceeding any stated finite proportion of the whole energy in either is very small. Suppose now the temperature to have become thus very approximately equalized at a certain time from the beginning, and let the motion of every particle become instantaneously reversed. Each molecule will retrace its former path, and at the end of a second interval of time, equal to the former, every molecule will be in the same position, and moving with the same velocity, as at the beginning; so that the given initial unequal distribution of temperature will again be found, with only the difference that each particle is moving in the direction reverse to that of its initial motion. This difference will not prevent an instantaneous subsequent commencement of equalization, which, with entirely different paths for the individual molecules, will go on in the average according to the same law as that which took place immediately after the system was first left to itself.

By merely looking on crowds of molecules, and reckoning

their energy in the gross, we could not discover that in the very special case we have just considered the progress was towards a succession of states, in which the distribution of energy deviates more and more from uniformity up to a certain time. The number of molecules being finite, it is clear that small finite deviations from absolute precision in the reversal we have supposed would not obviate the resulting disequalization of the distribution of energy. But the greater the number of molecules, the shorter will be the time during which the disequalizing will continue; and it is only when we regard the number of molecules as practically infinite that we can regard spontaneous disequalization as practically impossible. And, in point of fact, if any finite number of perfectly elastic molecules, however great, be given in motion in the interior of a perfectly rigid vessel, and be left for a sufficiently long time undisturbed except by mutual impact and collisions against the sides of the containing vessel, it must happen over and over again that (for example) something more than  $\frac{1}{10}$ ths of the whole energy shall be in one-half of the vessel, and less than  $\frac{1}{10}$ th of the whole energy in the other half. But if the number of molecules be very great, this will happen enormously less frequently than that something more than  $\frac{1}{10}$ ths shall be in one-half, and something less than  $\frac{1}{10}$ ths in the other. Taking as unit of time the average interval of free motion between consecutive collisions, it is easily seen that the probability of there being something more than any stated percentage of excess above the half of the energy in one-half of the vessel during the unit of time from a stated instant, is smaller the greater the dimensions of the vessel and the greater the stated percentage. It is a strange but nevertheless a true conception of the old well-known law of the conduction of heat, to say that it is very improbable that in the course of 1000 years one-half of the bar of iron shall of itself become warmer by a degree than the other half; and that the probability of this happening before 1,000,000 years pass is 1000 times as great as that it will happen in the course of 1000 years, and that it certainly will happen in the course of some very long time. But let it be remembered that we have supposed the bar to be covered with an impermeable varnish. Do away with this impossible ideal, and believe the number of molecules in the universe to be infinite; then we may say one-half of the bar will never become warmer than the other, except by the agency of external sources of heat or cold. This one instance suffices to explain the philosophy of the foundation on which the theory of the dissipation of energy rests.

Take, however, another case, in which the probability may be readily calculated. Let an hermetically sealed glass jar of air contain 2,000,000,000,000 molecules of oxygen, and 8,000,000,000,000 molecules of nitrogen. If examined any time in the infinitely distant future, what is the number of chances against one that all the molecules of oxygen and none of nitrogen shall be found in one stated part of the vessel equal in volume to  $\frac{1}{10}$ th of the whole? The number expressing the answer in the Arabic notation has about 2,173,220,000,000 of places of whole numbers. On the other hand, the chance against there being exactly  $\frac{2}{10}$ ths of the whole number of particles of nitrogen, and at the same time exactly  $\frac{2}{10}$ ths of the whole number of particles of oxygen in the first specified part of the vessel, is only  $4021 \times 10^6$  to 1.

#### APPENDIX.

##### *Calculation of probability respecting Diffusion of Gases.*

For simplicity, I suppose the sphere of action of each molecule to be infinitely small in comparison with its average distance from its nearest neighbour; thus, the sum of the volumes of the spheres of action of all the molecules will be infinitely small in proportion to the whole volume of the containing vessel. For brevity, space external to the sphere of action of every molecule will be called free space: and a molecule will be said to be in free space at any time when its sphere of action is wholly in free space: that is to say, when its sphere of action does not overlap the sphere of action of any other molecule. Let A, B denote any two particular portions of the whole containing vessel, and let  $a$ ,  $b$  be the volumes of those portions. The chance that at any instant one individual molecule of whichever gas shall be in A is

$\frac{a}{a+b}$ , however many or few other molecules there may be in

A at the same time; because its chances of being in any specified portions of free space are proportional to their volumes; and, according to our supposition, even if all the other molecules were in A, the volume of free space in it would not be sensibly diminished by their presence. The chance that of  $n$  molecules in the whole space there shall be  $i$  stated individuals in A; and that the other  $n-i$  molecules shall be at the same time in B, is

$$\left(\frac{a}{a+b}\right)^i \left(\frac{b}{a+b}\right)^{n-i}, \text{ or } \frac{a^i b^{n-i}}{(a+b)^n}.$$

Hence the probability of the number of molecules in A being exactly  $i$ , and in B exactly  $n-i$ , irrespectively of individuals, is a fraction having for denominator  $(a+b)^n$ , and for numerator the term involving  $a^i b^{n-i}$  in the expansion of this binomial; that is to say, it is—

$$\frac{n(n-1)\dots(n-i+1)}{1.2\dots i} \left(\frac{a}{a+b}\right)^i \left(\frac{b}{a+b}\right)^{n-i}.$$

If we call this  $T_i$ , we have

$$T_{i+1} = \frac{n-i}{i+1} \frac{a}{b} T_i.$$

Hence  $T_i$  is the greatest term, if  $i$  is the smallest integer which makes

$$\frac{n-i}{i+1} < \frac{b}{a};$$

this is say, if  $i$  is the smallest integer which exceeds

$$n \frac{a}{a+b} - \frac{b}{a+b}.$$

Hence if  $a$  and  $b$  are commensurable, the greatest term is that for which

$$i = n \frac{a}{a+b}.$$

To apply these results to the cases considered in the preceding article, put in the first place

$$n = 2 \times 10^{12},$$

this being the number of particles of oxygen; and let  $i = n$ . Thus, for the probability that all the particles of oxygen shall be in A, we find

$$\left(\frac{a}{a+b}\right)^{2 \times 10^{12}}.$$

Similarly, for the probability that all the particles of nitrogen are in the space B, we find

$$\left(\frac{b}{a+b}\right)^{8 \times 10^{12}}.$$

Hence the probability that all the oxygen is in A and all the nitrogen in B is

$$\left(\frac{a}{a+b}\right)^{2 \times 10^{12}} \times \left(\frac{b}{a+b}\right)^{8 \times 10^{12}}.$$

Now by hypothesis

$$\frac{a}{a+b} = \frac{2}{10},$$

and therefore

$$\frac{b}{a+b} = \frac{8}{10};$$

hence the required probability is

$$\frac{2^{26 \times 10^{13}}}{10^{10^{18}}}.$$

Call this  $\frac{1}{N}$ , and let  $\log$  denote common logarithm. We have

$$\log N = 10^{13} - 26 \times 10^{13} \times \log 2 = (10 - 26 \log 2) \times 10^{13} = 2173220 \times 10^6.$$

This is equivalent to the result stated in the text above. The logarithm of so great a number, unless given to more than thirteen significant places, cannot indicate more than the number of places of whole numbers in the answer to the proposed question, expressed according to the Arabic notation.

The calculation of  $T_i$ , when  $i$  and  $n-i$  are very large numbers, is practicable by Stirling's theorem, according to which we have approximately

$$1.2 \dots i = i^{i+\frac{1}{2}} e^{-i} \sqrt{2\pi},$$

and therefore

$$\frac{n(n-1) \dots (n-i+1)}{1.2 \dots i} = \frac{n^{n+\frac{1}{2}}}{\sqrt{2\pi} i^{i+\frac{1}{2}} (n-i)^{n-i+\frac{1}{2}}}.$$

Hence for the case

$$i = n \frac{a}{a+b},$$

which, according to the preceding formulæ, gives  $T_i$  its greatest value, we have

$$T_i = \frac{1}{\sqrt{2\pi n e f}},$$

where

$$e = \frac{a}{a+b} \text{ and } f = \frac{b}{a+b}.$$

Thus, for example, let  $n = 2 \times 10^{13}$ ;

$$e = .2, f = .8,$$

we have

$$T_i = \frac{1}{800000 \sqrt{\pi}} = \frac{1}{1418000}.$$



This expresses the chance of there being  $4 \times 10^{11}$  molecules of oxygen in A, and  $16 \times 10^{11}$  in B. Just half this fraction expresses the probability that the molecules of nitrogen are distributed in exactly the same proportion between A and B, because the number of molecules of nitrogen is four times greater than of oxygen.

If  $n$  denote the molecules of one gas, and  $n'$  that of the molecules of another, the probability that each shall be distributed between A and B in the exact proportion of the volume, is

$$\frac{1}{2\pi ef \sqrt{nn'}}$$

The value for the supposed case of oxygen and nitrogen is

$$\frac{1}{2\pi \times 16 \times 4 \times 10^{12}} = \frac{1}{4021 \times 10^6},$$

which is the result stated at the conclusion of the text above.

*XXX. A Detector for Spark in Hertz's Resonator.*

*By W. LUCAS, M.A., and T. A. GARRETT, M.A.\**

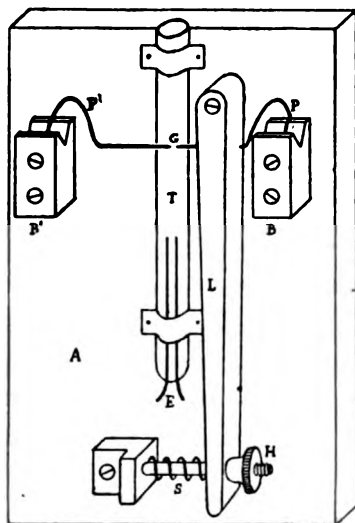
SINCE Prof. Hertz published his classical researches on electrical oscillations several methods have been devised for showing some of the principal experiments to a number of people simultaneously.

It seemed to us that a very direct method of doing this would be to make the spark of the resonator ignite an explosive mixture of gases. After making many experiments we find that a very convenient form of apparatus for effecting this is the following:—A long strip of wood (not shown in the figure), having near its ends two projecting blocks with V-cuts in them, is supported in a horizontal position, and to the middle of it is screwed the base-board A, its position being vertical. B and B' are two more blocks with V-cuts in them. The four blocks are arranged in such a way that the V-cuts in them are in the same straight line. In the V-cuts of the four blocks the two straight wires which form the resonator rest. The spark-gap G is between the ends of the platinum wires P and P'; these are led down into the V-cuts in B and B' as shown, so that the resonator wires rest in contact with them. P is fixed firmly to the wooden lever L, so that the size of the spark-gap can be easily adjusted by turning the milled head H, against which the lever is pressed by the

\* Communicated by the Authors.

spiral spring S. To allow for this adjustment P is bent as shown, and P', though fixed permanently, is also bent, so that both parts of the resonator may be symmetrical. With this arrangement one pair of resonator wires can be very readily replaced by another pair of a different size.

A Detector for Spark in Hertz's Resonator.



T is a glass tube open at the top. Its lower end is closed and two platinum electrodes E are sealed into it. Two small holes are bored through it diametrically opposite to each other, through which the platinum wires P and P' can pass freely. This tube is partly filled with hydrochloric acid, and the electrodes E are connected with a battery so as to generate an explosive mixture of hydrogen and chlorine. If the resonator sparks when enough gas is present in the tube, an explosion is produced.

In order that an explosion may be produced by every spark, the time required to fill the tube with the quantity of gas requisite for an explosion must be less than the interval of time between two sparks. If this interval is small, the quantity of gas requisite for an explosion must be small and it must be generated quickly. Now in order that the quantity of gas requisite for an explosion may be small, the diameter of the tube must be small and the spark-gap must be near the surface of the electrolyte. We find, however, that when under these circumstances the gas is generated quickly, an

explosion very rarely takes place, owing to the fact that liquid is carried up to the spark-gap by the rush of gas, and a minute drop almost always adheres to the ends of the wires forming the spark-gap, so that no spark, and consequently no explosion, is produced.

This difficulty, however, can be easily overcome by connecting the two halves of the resonator with a battery of three or four cells, so that as soon as a minute drop is formed across the spark-gap it is at once dissipated by the current which passes through it. If the battery connexions are made at nodes, the proper working of the resonator does not seem to be interfered with, so that the battery may remain in permanent connexion with it.

Of course the same battery may be used both for getting rid of the drop and for generating the explosive mixture of gases, the circuit which is completed by the drop in the spark-gap being a shunt on the circuit through the electrolyte. When it is desired to work with a very small spark-gap, we have found it very convenient to include a rough galvanometer in the former circuit, as a small spark-gap can then be very easily made by screwing up H, stopping directly a deflexion is obtained, and then screwing H back very slightly so as just to break the circuit.

In our first experiments we used dilute sulphuric acid as the electrolyte instead of hydrochloric acid; but we found that when the spark was very small, it failed to explode the mixture of oxygen and hydrogen produced. When, however, hydrochloric acid is used, so far as we have observed, every spark, even the smallest we have been able to obtain, produces an explosion, provided of course that the tube is properly filled with gas.

In conclusion, it might be well to add that the tube which we have found to work very satisfactorily is 16 centim. long and 8 millim. in diameter (inside), the spark-gap being about 5 centim. from the top.

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XXXI. *Dynamical Illustration of the Isothermal Formula.*  
By LADISLAS NATANSON, *Phys.D., Lecturer on Natural Philosophy, University of Cracow*.\*

IN the Kinetic Theory of Matter it is our object (as will, I think, be generally admitted) to imagine a dynamical model of some definite state of matter and to investigate the properties of the mechanism conceived.

\* Communicated by the Author.

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A system of hard elastic spheres, which exert upon one another purely collisional forces, has been found to be in many respects an adequate dynamical representation of what is called an *ideal* gas. The laws of ideal gas-pressure cannot, however, be accounted for, unless the spheres, or molecules, of which the body is supposed to consist are assumed to be infinitely small.

Now we know that, in order to explain the properties of *real* or imperfect gases, it is *not* sufficient to correct the original theory under this head solely, *i. e.* to consider the molecules as bodies of some small but definite size. Van der Waals was led therefore to investigate the effect of attractive or cohesive forces, which he supposed to operate between molecules independently of impulsive forces, generated on collision. Accordingly in his equation two correctional quantities appear, determined respectively by both of these distinct kinds of molecular interference. To my mind such a cumulation of essentially heterogeneous assumptions is utterly unsatisfactory; and it certainly fails to connect the properties to be explained with *one* dynamical fact only. Hence, I venture to think, we have to take some broader view of the nature of molecular interaction.

On the other hand, although no serious discordance is likely to arise as to the highly important *role* of Van der Waals's theory in modern thermodynamical science, it must nevertheless be affirmed that his equation does not apply to known facts with due approximation, so that the kinetic conception on which it is founded may be said to be disproved.

1. The fundamental assumption I propose to examine is, that the molecules of a gas may be taken as mere material points, which exert upon one another certain forces every time the distance between them becomes equal to, or less than, a given limit,  $R$  say. Whenever two molecules approach within distance  $R$ , they will be said to undergo encounter; and the moment the distance becomes again greater than  $R$  will be taken as the ending moment of entanglement. When two or more molecules are thus under mutual interaction, I call them a molecular system; I shall confine myself, however, at first to the consideration of bimolecular systems by supposing the ratio of systems of any higher degree of complexity to be small enough to be neglected.

Consider a volume  $V$ , in which  $N$  points or molecules are constantly moving. Let  $Nf(v)dv$  denote the number of molecules whose velocities lie between  $v$  and  $v+dv$ . These we shall call "*v*-molecules"; and similar abbreviations will be used in other cases. Among the members of that class con-

sider a single molecule  $a$ ; let there be in volume  $V$  a number  $Nf(v, w) dv$  of molecules which are moving with relative velocity  $\geq w$  and  $\leq w + dw$  with respect to molecule  $a$ . Call  $\psi$  the acute angle between the  $w$  and  $R$  directions at the beginning moment of encounter. It is then easily proved that the molecule  $a$  will suffer per unit time

$$\frac{2\pi NR^2}{V} w F(v, w) \sin \psi \cos \psi dv dw d\psi \quad . \quad . \quad (1)$$

encounters of the  $w, \psi$  description. Now in a large class of laws of force the duration-time of entanglement is determined by the values the two variables  $w, \psi$  assume at the beginning moment of encounter; and from the following it will be obvious that our deduction would apply with but formal alterations to the more general case, when further variables are required. Let then  $\tau$  be the duration-time of entanglement; every encounter of the above class (1) will belong to the class of  $\tau$ -encounters. These encounters are happening with the concurrence of molecule  $a$ ; but the same being true for every other member of the  $v$ -class, and the state of things in the whole mass being assumed to be steady, we shall find the number of encounters which at any time are just happening in the volume considered by multiplying (1) by  $\tau$  and by  $Nf(v) dv$ , by integrating, and halving. Let  $\frac{1}{2} Nc$  represent that number;  $c$  therefore is taken to mean the ratio of molecules which belong at a given time to molecular systems. The number of free molecules is equal to  $N(1-c)$  and

$$c = \frac{2\pi NR^2}{V} \iiint \tau w f(v) F(v, w) \sin \psi \cos \psi dv dw d\psi \quad . \quad (2)$$

2. Let us now proceed to the application of the virial equation. In this equation we have to introduce, it is well known, certain average values of the kinetic energy and the virial, and these averages are to be found in the following way. We have to write down the value of the kinetic energy and the virial for every molecule, to sum them up, to continue this process during some long period of time, and to average at last all the instantaneous sums we have computed. Now, since the state of the gas is steady, we are justified in applying the theorem directly to the instantaneous sums of kinetic energy and virial, which cannot differ materially from their time-averages. There is no difficulty in performing the summation as far as the kinetic energy of free molecules and the virial of external pressure (no other external forces being admitted) are concerned; but terms relating to molecular

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systems require closer examination. Suppose  $Q$  to represent a quantity characteristic for a system in a given state; *i. e.* a function, *first* of the initial conditions of encounter, and secondly of the time  $t$ , which in the system under consideration has elapsed from the beginning moment of encounter. If we multiply the above number (1) by

$$Nf(v) dv dt, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

we shall have the number of encounters which occurred at moments lying infinitely near one another and under initial conditions differing but infinitely little. In all these encounters the simultaneous values of  $Q$  are practically equal, hence

$$NQf(v) dv dt, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

multiplied by (1), is the instantaneous  $Q$ -sum for the  $v, w, \psi, t$ -subclass considered; and the sum for the  $v, w, \psi$ -class is found by integration from 0 to  $\tau$ . Now let  $\bar{Q}$  denote the mean value the variable quantity  $Q$  assumes in the course of the encounter; since, then,

$$\int_0^\tau Q dt = \bar{Q} \tau, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the  $Q$ -sum for the total mass of gas is seen to be

$$\frac{\pi N^2 R^2}{V} \iiint \bar{Q} \tau w f(v) F(v, w) \sin \psi \cos \psi dv dw d\psi. \quad (6)$$

3. The kinetic energy of two molecules suffering mutual interaction we shall divide in two parts, which will correspond respectively to the mutual relative motion of the molecules and to the motion of their centre of inertia. Call  $L$  the mutual relative kinetic energy of both molecules and  $S$  the virial of the forces between them; then, with the above notation for averages, and with  $m$  to denote the masses of the points (supposed to be equal), we have

$$\bar{L} - \bar{S} = \frac{mwR \cos \psi}{2\tau}, \quad . \quad . \quad . \quad . \quad (7)$$

by a theorem which is closely connected, but cannot be said to be identical with the ordinary Virial-theorem. (See Wiedemann's *Annalen*, vol. xxxiii. p. 698.)

4. The virial-equation is now easily constructed. If we use  $E$  to denote the mean kinetic energy of a free molecule,  $E_c$  the mean kinetic energy of the centre of inertia of a bimolecular system, and  $p$  the external (normal and uniform) pressure, we find

$$\frac{3}{2}pV = N(1-c)E + \frac{1}{2}NcE_0 + \frac{\pi N^2 R^2}{V} \iiint (\bar{L} - \bar{S}) \tau \omega f(v) F(v, w) \sin \psi \cos \psi \, dv \, dw \, d\psi, \quad (8)$$

and this takes by (7) the form

$$\frac{3}{2}pV = NE - \frac{1}{2}Nc(2E - E_0) + \frac{N\omega}{2V} \iiint \frac{1}{2}mw^2 \cdot f(v) F(v, w) \, dv \, dw, \quad (9)$$

where

$$\omega = \frac{4}{3}\pi NR^3. \quad (10)$$

The double integral in (9) is seen to represent (apart from the factor  $N\omega/2V$ ) the mean value of the relative kinetic energy for all *ideal* combinations of two points we are able to imagine throughout the gaseous mass; but it is clear that this mean is essentially different from the mean relative kinetic energy for interacting molecules, or molecular systems. It follows that we have to write  $(2E - E_0)$  for the value of the double integral. For suppose we are computing all possible imaginary pairs of molecules throughout the gas; the frequency of *systems* in which true physical connexion occurs among our ideal pairs cannot depend upon the velocity of the centre of inertia of the pairs, hence  $E_0$  added to the mean value of  $\frac{1}{2}mw^2$  must be equal to  $2E$ . We have, then,

$$\frac{3}{2}pV = NE + \frac{1}{2}N(2E - E_0)\left(\frac{\omega}{V} - c\right). \quad (11)$$

Now write for simplicity,

$$1 - \frac{E_0}{2E} = \epsilon \quad (12)$$

and

$$\epsilon\left(\frac{\omega}{V} - c\right) = \frac{b}{V}, \quad (13)$$

so that

$$b = 2\pi\epsilon NR^2 \iiint \left\{ \frac{2R \cos \psi}{w} - \tau \right\} \omega f(v) F(v, w) \sin \psi \cos \psi \, dv \, dw \, d\psi; \quad (14)$$

equation (11) takes the form

$$\frac{3}{2}pV = NE \left(1 + \frac{b}{V}\right), \quad (15)$$

similar to those obtained by Van der Waals, Lorentz, and other authors. It would seem, however, to deserve here special attention, that  $b$ , according to (14), may be either positive, or zero, or negative, as the law of force varies; and still more suggestive is the further possibility of  $b$  changing its sign, for a given law of force, at some definite temperature or temperatures.

For passive molecules  $\tau = 2R \cos \psi / w$  and  $b = 0$ ; for hard elastic spheres  $\tau = 0$  and  $b = \frac{1}{2}w$ , because, as will immediately be shown,  $\epsilon = \frac{1}{2}$ . This is in accordance with Van der Waals's result, since his molecular volume corresponds to  $\frac{1}{3}w$ .

5. Let us consider the number of encounters which happen per unit time between molecules of class  $v_1$  and class  $v_2$  respectively with the further restriction of the angle between the  $v_1$ - and  $v_2$ -directions being  $\geq \lambda$  and  $\leq \lambda + d\lambda$ . If, for reasons presently to be seen, we substitute  $v^2\phi(v)$  for  $f(v)$ , as written in the above, we may put that number

$$= \frac{1}{2}\pi N^2 R^2 v_1^2 v_2^2 w \sin \lambda \phi(v_1) \phi(v_2) dv_1 dv_2 d\lambda. \quad (16)$$

Now, in (16), we introduce the relative velocity  $w$  of the two molecules, and the velocity  $V$  of their centre of inertia, by means of

$$v_1^2 + v_2^2 = \frac{1}{2}w^2 + 2V^2 \quad (17)$$

and

$$v_1^2 + v_2^2 - 2v_1 v_2 \cos \lambda = w^2; \quad (18)$$

it follows that the number of  $v_1, w, V$ -encounters per unit time is

$$\pi N^2 R^2 v_1 w^2 V \phi(v_1) \phi(v_2) dv_1 dw dV. \quad (19)$$

We have next to integrate this with respect to  $v_1$

from  $v_1 = \sqrt{\frac{1}{4}w^2 + V^2 - wV}$  to  $v_1 = \sqrt{\frac{1}{4}w^2 + V^2 + wV}$ ,

and this may be done directly, the result being simply  $wV$ , because the product  $\phi(v_1) \cdot \phi(v_2)$ , by a method of proof originally given by Clerk Maxwell and since frequently used in the Kinetic Theory, may be shown to be of the form  $\psi(w)\Psi(V)$ . Hence the number of  $w, V$ -encounters per unit time is

$$\pi N^2 R^2 w^3 V^2 \psi(w) \Psi(V) dw dV, \quad (20)$$

and the law of distribution for the  $V$ -velocities is expressed by  $V^2 \Psi(V) dV$  with a proper constant prefixed. Now the only relation between  $v_1, v_2, w$ , and  $V$  is clearly that given by equation (17). From this equation, then, and from

$$\log \phi(v_1) + \log \phi(v_2) = \log \psi(w) + \log \Psi(V), \quad (21)$$

the form of the functions may be inferred, and the conclusion may be drawn that the mean value of  $V^2$  is equal to half that of  $v_1^2$  or  $v_2^2$ . Hence

$$E = E_e \text{ and } \epsilon = \frac{1}{2}. \quad (22)$$

This result shows, besides, that we are justified in taking  $NE = \frac{3}{2}Rt$  say, where  $t$  is the absolute thermodynamical temperature.



6. We shall make no attempt to recognize the true law of force acting between the molecules ; but it is obvious that  $b$  does not depend upon  $V$  any further, so that, with  $\rho$  to denote the density of the medium, our equation becomes

$$p/\rho = Rt(1 + T_1\rho), \quad . . . . . (23)$$

$T_1$  being a function of the absolute temperature.

Now by similar considerations which, I think, it is unnecessary to reproduce at length, we may generalize our deduction by taking higher systems of molecules into account. Suppose we stop at  $i$ -molecular systems and neglect the number of those formed by  $i + 1$  molecules ; then the equation will be

$$p/\rho = Rt(1 + T_1\rho + T_2\rho^2 + \dots + T_{i-1}\rho^{i-1}) \quad . . (24)$$

(the  $T$ 's being functions of  $t$ ), and is thus seen to be of the general type suggested by Maxwell ('Scientific Papers,' vol. ii. p. 407) and recently supported by Lord Rayleigh ('Nature,' vol. xlv. p. 81). Equations of that kind are carefully discussed in Thiesen's elaborate paper in *Wiedemann's Annalen*, vol. xxiv. p. 467 ; see also *ibidem*, vol. xxxiii. p. 701. It would seem therefore that, in the proximity of the critical state, double and triple molecules are prevalent ; while (if we adopt a recent suggestion from Blümcke, *Zeitsch. für phys. Chemie*, vol. viii. p. 562) in the proximity of the solid state even the effect of systems consisting of eight molecules each may become traceable.

### XXXII. On a Permanent Magnetic Field.

By W. HIBBERT, A.I.E.E., F.I.C.\*

IN the electrical laboratory of the Polytechnic Institute, Regent Street, the earth's magnetic field varies so much that it cannot be assumed as a basis for reasonably accurate measurement. For this reason it was formerly my habit to give students a certain bar-magnet as a temporary standard, the number of lines passing out of the bar being determined afresh from time to time. This magnet was an old one, and its varied experience (now described under the term "ageing") had given it an approximate constancy. The constancy was, in fact, good enough to suggest the possibility of getting a really permanent magnet. I therefore made some tentative efforts to ascertain the effect of slight variations in the hardness and temper of steel on its magnetic properties, with the result that I found the subject too great for my resources.

\* Communicated by the Physical Society : read December 4, 1891.

But the growth of the modern idea of a magnetic circuit suggested the possibility of achieving my purpose in a way that would be largely independent of the peculiarities of different brands of steel, as well as of the various physical conditions caused by differences in tempering.

I therefore provided a short straight bar-magnet with a couple of arched pole-pieces, of such length and sectional area that there was left between them a narrow air-gap of very small magnetic "resistance." A very flat coil of wire thrust in or out of this gap gave electromagnetic impulses whose value was fairly constant. Experience with these simple instruments led me to believe that a more rigorous application of the principle would give a truly permanent magnetic field. How far this has been realized will appear from the considerations which I now have the honour to submit to the Society.

The first design that at all approximated to a closed magnetic circuit consisted of a cylindrical steel rod with hemispherical pole-pieces. For reasons into which I need not go, this has been superseded by the following modification.

Fig. 1.

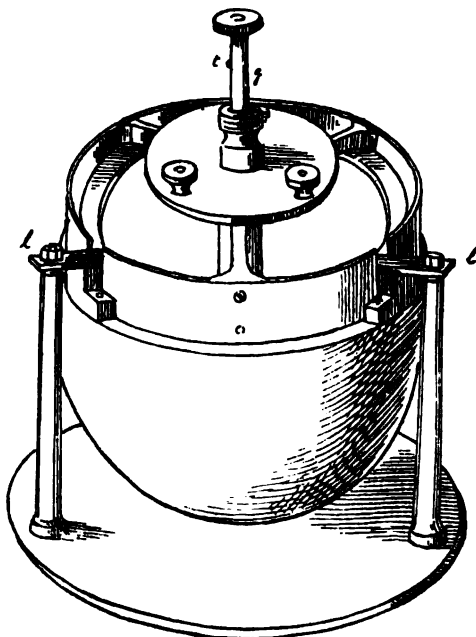
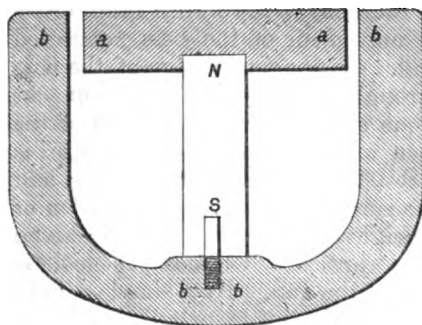


Fig 1 is a general view of the instrument. Fig. 2 is a

vertical section of the magnetic circuit. In this, *NS* is a cylindrical steel rod,  $2\frac{1}{4}$  inches long and 1 inch in diameter, attached to two cast-iron pole-pieces. The upper pole-piece, *aa*, is a circular disk, 4 inches in diameter and  $\frac{5}{8}$  inch thick, carefully bored to fit the upper end of *NS*. The lower pole-piece, *bb*, is nearly hemispherical, and about  $\frac{1}{2}$  inch thick in the wall. This is attached to the steel rod by means of an iron pin, let into *NS* and screwed into *bb*.

Fig. 2.



The opposed faces of the pole-pieces are carefully turned in the lathe, so as to leave between them a circular air-gap less than  $\frac{1}{16}$  inch wide.

The above description gives the form and dimensions of the magnetic part of the instrument. It is magnetized after being put together by a current sent through a coil wound on the steel rod.

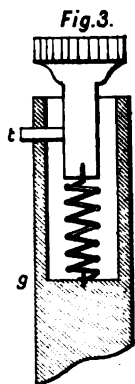
The other parts consist of :—

(1) Mechanical arrangements which will rigidly preserve the pole-pieces in position.

(2) Arrangements which will carry and guide a coil of wire as it is thrust through the field in the very narrow air-gap. Screwed to the upper surface of the disk *aa* is a brass casting with three projecting lugs *ll* (fig. 1). These lugs are screwed both to small blocks attached to the hemispherical pole-piece, and also to the tops of three brass pillars (fig. 1).

The coil is wound in a shallow groove cut on the outside of a brass ring, which is turned thin enough in the wall to slide freely through the air-gap. Attached to its upper edge are three arms which radiate from a central boss, the latter sliding up or down on the central guide-rod *g* (fig. 1). The radial arms support an ebonite disk on which are fixed the terminals of the coil.

At the upper end of the guide-rod *g* is an arrangement for allowing the ring to fall whenever the experimenter desires. The upper end of *g* is bored out (fig. 3), and a horizontal slot is cut in the thin wall thus made. In the inner space and connected with the milled head is a rod, from the side of which projects a tooth *t* passing through the slot, whilst from the lower end passes a spiral spring also fixed into the body of *g*. The tooth *t* is thus kept in a definite position, from which it can be moved aside either by a rotation of the milled head, or by the upward movement of the boss connected with the ring. On the inner edge of the boss is a slot through which *t* can pass, but cut slightly on one side of the zero position of the tooth. When an electromagnetic impulse is desired the coil is raised so that the boss, and therefore the ring, rests on *t*. The position of *t* and the height of the ring are so chosen that when the ring is at rest on *t* the coil is altogether above the gap. By a simple rotation of the milled head the coil can be made to fall through the field at any desired moment. The electromagnetic impulse then given to the circuit is, of course, equal to the number of lines interlinked with the coil during the fall, multiplied into the number of turns of wire in the coil.



Three instruments of the type just described have been made and tested. The means adopted for testing are not the best that could be specified for the purpose. They were chosen because they give reasonable accuracy, and yet allow of a fair number of observations being taken in a limited time.

The method was to compare two throws of a galvanometer-needle, one produced by the discharge of a condenser, the other produced by the magneto-inductor.

The condenser employed was a mica condenser of 0.333 microfarad capacity. The potential difference for charging was obtained from four accumulators, whose electromotive force was determined by comparison with a Latimer-Clark cell, the comparison being made by the potentiometer method.

Having first taken a fair number of observations from the condenser, a corresponding number were taken from the magneto-inductors, the resistance in circuit with each being adjusted till the throw was practically the same as that obtained from the condenser.

I decided on this because it allowed me to use an ordinary damped reflecting-galvanometer. The object being simply

to test constancy, it was evident that the subsequent tests would be very much like the first, and that by the above method of working I might neglect damping, and also any consideration of the law of the galvanometer deflexion.

As the observations run through summer and winter they had to be corrected for temperature variation. The coefficients used were those now generally accepted, namely:—For the Latimer-Clark cell 0.077 per cent. per 1° C; for the copper wire of the galvanometer 0.38 per cent. per 1°; and for the German-silver resistances 0.044 per cent. per 1°.

It now remains to give the results obtained. As my present purpose is simply to show how far constancy of field has been obtained, it is not necessary to give many details. Before giving the results it will be proper to state the chief differences between the instruments numbered I., II., and III. in the Table.

*Hemisphere No. I.*—Air-gap a little more than  $\frac{1}{8}$  inch and not quite uniform. Magnetized by flashing current from four accumulators, July 29, 1890. Heated and cooled several times on different days. Very small decay to August 11, on which day the number of lines = 21,007. Next day, August 12, 1890, lines = 21,120. Seven months later, March 14, 1891, lines = 21,035. Accident to coil caused me to take to pieces and magnetize afresh. A current flashed through at a temperature of about 50° C.

*Hemisphere No. II.*—Most highly finished. Air-gap rather less than  $\frac{1}{8}$  inch. Magnetized by flashing. Lines about 34,000. Nearly 50 per cent. greater than in I. This showed tendency to fall. I therefore adopted the method known as “reducing,” by sending reverse current through magnetizing coil. Reduction of field about 5 per cent.

*Hemisphere No. III.*—Magnetic system not so well supported as in two previous instruments. Magnetized by flashing current, and then “reduced” about 20 per cent.

The figures in the column headed “No. of Lines” are obtained by the expression

$$N = \frac{100 \text{ CVR}}{t} \cdot \frac{d'}{d};$$

where C = capacity of condenser in microfarads,

V = potential difference in volts,

R = resistance in circuit with magneto-coil,

t = number of turns of wire on magneto-coil,

d', d = throws from magneto-inductor and condenser respectively.

The factor 100 translates from practical to absolute units.

Date.	Temperature of Inductor.	Lines in Inductor Field.		
		No I.	No. II.	No. III.
April 16, 1891.....	50 C.	22,030		
" " " .....	20	21,790		
" 22 " .....	12.5	21,730		
" 23 " .....	13.5	21,710	32,360	
May 8 " .....	16.5	21,710	32,420	
" 23 " .....	13	21,680	32,330	
" 27 " .....	13.5	.....	.....	29,140
" 30 " .....	16	21,720	32,410	29,290
June 6 " .....	18	21,720	32,380	29,270
" 12 " .....	22	21,780	32,470	29,260
" 29 " .....	21.5	21,720	32,345	29,290
July 10 " .....	19	21,790	32,510	29,500
" 27 " .....	20	21,700	32,470	29,550
" 31 " .....	17.5	21,780	32,460	29,530
Sept. 22 " .....	16	21,690	32,400	29,470
Nov. 10 " .....	13	21,700	32,400	29,480
Density of lines in air-gap per sq. cm. }	.....	515	770	700

In discussing the figures it must be remembered that high accuracy was not attainable at the time of working. The observations were all made in comparatively brief intervals of leisure, and it is likely that the probable error is about 1 in 300 or 400.

There is practically no evidence of magnetic decay in seven months. Such small changes as are indicated point the other way, but I am inclined to attribute most of them to slight inaccuracy of the temperature-correction for the resistances of the circuit.

The two instruments that were reduced by a demagnetizing current (Nos. II. and III.) show a tendency to rise. This tendency is most marked in the instrument which was reduced most. It is evident that only a slight reduction is to be allowed.

No. I., which was magnetized warm, but not "reduced," fell while cooling, and then showed a very slight tendency to increase. It is better than the other two, and is constant enough to be used for any purpose for which an earth inductor is employed.

Nothing is here said of the temperature variation of this magnetic field\*. I have made some observations on that

\* Magnetic field is of course not the right name. The instrument raises once again the question of naming the quantity sometimes called "total field," "total induction," or so many "gausses."

point, and found it very small, but as the tests were made with hastily-adjusted appliances, I have thought it better to reserve the matter for further investigation. The temperature range involved in the Table is  $10^{\circ}\text{C}.$ , but the figures cannot be used for deducing the temperature-coefficient because of the other sources of error. I am inclined to think that the temperature variation of the condenser (which has not been applied to the calculations) practically neutralizes that of the inductor.

In addition to the evidence of constancy afforded by the Table, there are in my note-books several facts which point the same way. Of these I shall mention only one.

It is well known that magnetic decay is most pronounced just after magnetization, especially if the magnet is subjected to vibration. In several early cases I tested the effect of vigorous blows during and immediately after magnetization, but the evidence of loss was generally very feeble, and in some cases not measurable. In this connexion it may be worth noting that the brass ring which carries the coil is fairly heavy, and that when it falls it produces an appreciable blow. Each of the three instruments has been subject to this shock hundreds of times, but has shown no sign of decay under it.

Perhaps I may be permitted to say that I do not advance the principle of the magnetic circuit as at all novel. It has already been embodied in several well-known applications. But I believe the idea is here made subservient to new purposes.

As a material embodiment of a standard of magnetism (magnetic lines, gaussses, or whatever else may be the right name) I find it helpful to many students. For this reason I propose to adjust future instruments of this size to a round number of lines, say 20,000 or 25,000, which will facilitate calculations arising out of their use.

The instrument is a most convenient standard for measuring magnetic quantities, whether it be the lines in any other magnet or the vertical and horizontal components of the earth's field. I am trying to use it for developing a new method of determining these quantities.

It enables me to simplify the magnetometer method for determining magnetic permeability. Over the ordinary magnetizing coil I wind a sufficient number of turns of a secondary. The coil with its core is fixed in *any* position that is convenient, and the *relative* number of lines determined by the magnetometer deflexion in the usual way. At the end of the magnetization the total *absolute* number of lines (corresponding to the maximum magnetometer deflexion) is found by taking

a throw from the secondary coil when the magnetizing current is reversed. This throw is then compared with that obtained from one of the inductors. By this method one is relieved from measuring distances whose cube &c. enters into the formula for reducing the observations.

I ought not to close without acknowledging the help given all through by the instrument-maker, Mr. G. Bowron, one of whose workmen, Mr. Collins, suggested the convenient method of release described in the paper.

### XXXIII. *Notices respecting New Books.*

*Annals of British Geology*, 1890. By J. F. BLAKE, M.A., F.G.S.  
8vo. 352 pages. Dulau and Co. London, 1891.

THE author, who is the President of the Geologists' Association, defines this work as "a critical digest of the publications and account of papers read during the year—with personal items." The subject-matters are limited to notes and memoirs supplied by British geologists in 1890, whether actually published, or merely announced in the Reports and Proceedings of Societies as having been read. In the former case careful and often full abstracts are here given; and the latter (the nos. of which are enclosed in square brackets) serve to indicate the lines of thought and research taken by numerous observers and thinkers, the results of which may be looked for in future Journals. Papers, maps, and sections (657), having relation to the British Isles, are mentioned at pages 1-299; papers on foreign Geology, published in Britain (95), are to be found at pages 299-339.

General, including physical and theoretical, Geology comes first in the subdivisions of subjects; then stratigraphical geology according to successive formations from the oldest to the newest; next palæontology, with vertebrates and invertebrates in zoological order, down to sponges and microzoa; palæobotany, mineralogy, petrology, and economics succeed; maps and sections follow; and then foreign geology as treated in British papers, in order like the above. Lastly, there are what are termed "Personal Items," as to the Geological and other Societies,—their Presidents, new Fellows, and Awards,—also the holders of Geological Professorial Chairs,—the Staff of the Geological Survey of Great Britain and Ireland, and of the Geological and Mineralogical Departments of the Natural-History Branch of the British Museum, and other matters. An Index of Authors, and another of Periodicals mentioned in the text, complete this comprehensive and well-arranged work.

More or less complete bibliographic lists of geological books and memoirs are supplied periodically in several countries (England, France, Germany, Russia, United States, &c.); but a separate



annual catalogue raisonné of the works produced in each country would, the author suggests, be more satisfactory and useful, and more likely to be well elaborated. He has, therefore, given much time and energy to the production of the present work, which is not a meagre catalogue with contracted notes on the contents of papers, pamphlets, and books, but is intended to be readable and useful to scientists, conveying all the important facts and arguments brought out in the papers, and thus indicating the actual progress of Geology in all its branches, as advanced or treated of in the one Country under notice.

The British area with its actual epitome of geological phenomena, and its numerous local Societies studying the same, and very often taking foreign geology also into their consideration, is peculiarly fit to supply an annual series of both practical and theoretical observations, worthy of full notice in such a periodical volume as J. F. Blake's '*Annals of British Geology*' now before us.

In many of the abstracts composing this volume, for 1890, the author offers critical observations, enclosed in square brackets [ ], where the facts seem to be obscure, the arguments incomplete, or the conclusions not proved, the statements thus appearing to be obviously erroneous or inconsistent. Such interpolated remarks, if sound and well directed, may be valuable as well to the writer criticised as to the reader of the bibliography; and even mistaken criticism, the author thinks, may in some cases be better than none, being merely personal opinion open to correction.

We expect that few geologists, besides the Author, could be found equal to the all-round work of making such fair and lucid abstracts of numerous papers on all the subdivisions of the science as those in the present volume. A sound acquaintance with all the subjects has made him also an able critic, rarely influenced by his personal views. Thus the strictures in Article no. 440, p. 208, deserve notice; and in the Articles nos. 138 & 139, pp. 52-56, several apt and just criticisms come in where wanted to support the claims of the Murchisonian against the Sedgwickian school, respecting the history of the "Silurian-and-Cambrian" controversy, and the determination and naming of the subdivisions of those palæozoic strata. On the other hand, in Article no. 259, at page 146, the first half of the critique does not show a mastery of the sections referred to. In Article no. 665, at pp. 305, 306, the term "Coralline Limestone" might, according to the fossils mentioned, have been accompanied with the critical correction [Nulliporan Limestone]. So also in Article no. 249, at pp. 128, 129, the critical correction [Polyzoan Crag] might advisedly have followed the term "Coralline Crag."

We may note that there are very few clerical errors, considering the technical character of the text, and the many lists of strata, fossils, analyses, &c. The book is well and clearly printed; and with its varied and carefully collected information, as noticed above, must be of great use to geologists in many ways. We hope that it will be well supported, and continued; so that succes-

sive volumes may supply an adequate record of the progress of British Geology, which is an important element in the studies of geologists all over the world. To local workers and country Societies it will be of great service, readily giving them a wide view of the science, and bringing their publications to the knowledge of the general body of geologists.

#### XXXIV. *Intelligence and Miscellaneous Articles.*

ON THE REFRACTION OF SOUND, AND ITS VELOCITY IN POROUS SUBSTANCES PERMEABLE TO SOUND. BY N. HESEHUS.

THE author gives the name of bodies *permeable* to sound to porous bodies such as wadding, eiderdown, sponge-shavings, &c., which are reputed to be bad conductors of sound, which they transmit more or less freely by their pores filled with air. Experiments on the propagation of sound in this class of bodies present great interest in consequence of the analogy with the propagation of light in transparent media, and of electrical vibrations in dielectrics.

As the velocity of sound in the interstices of a porous body is less than in air, it is to be expected that by means of these bodies we could bring about the refraction of sound. A hemisphere, 25 centim. in diameter, of metal gauze filled with ebonite shavings, and closed by a plane sheet of the same gauze, behaved like a plano-convex lens in reference to the sounds of a Galton's whistle. The experiment may even be repeated in a lecture provided we use a Gore's sensitive flame to observe the strengthening and enfeeblement of the sound. The well-known formula of lenses enables us to calculate the refractive index of, and therefore the velocity of sound in, the material of the lens as a function of its principal focal distance and its radius of curvature. The velocity, thus determined, decreases when the density of the substance of the lens is increased by placing more shavings in the same envelope. The velocity  $v$  may be calculated by the following empirical formula,

$$v = 343(1 - \delta)^{0.322\delta - 5},$$

in which 343 (metres) is the velocity of sound in air at 18° C.,  $\delta$  the quotient of the mass of the shavings filling the lens by the mass of a lens of the same dimensions of solid ebonite, so that  $1 - \delta$  expresses the quotient of the volume of air contained in the pores by the volume of the lens.

The value of the wave-length of the sound employed varied in the experiments of the author between 24 millim. and 60 millim., and that of  $\delta$  between 0.0356 and 0.1441; the velocities calculated by the formula of lenses from these data being comprised between 261 metres and 146 metres.—*Journal de Physique*, Dec. 1891 from *Société Physico-Chimique Russe*.

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XXV. On the Theory of Long Waves and its Application to the Tidal Phenomena of Rivers and Estuaries. By J. McCOWAN, M.A., B.Sc., Assistant Lecturer on Natural Philosophy, University College, Dundee .....	250
XXVI. On the Intensity at the Focal Point of a Telescope, when the Object-glass is covered by a Diaphragm pierced with Circular Apertures. By JAMES WALKER, M.A., Demonstrator at the Clarendon Laboratory, Oxford .....	266
XXVII. Struts and Tie-Rods with Lateral Loads. By Professor JOHN PERRY, D.Sc., F.R.S. ....	269
XXVIII. The Hypothetical Tetrachloride of Manganese. By SPENCER UMFREVILLE PICKERING, F.R.S. ....	284
XXIX. The Kinetic Theory of the Dissipation of Energy. By Sir WILLIAM THOMSON .....	291
XXX. A Detector for Spark in Hertz's Resonator. By W. LUCAS, M.A., and T. A. GARRETT, M.A. ....	299
XXXI. Dynamical Illustration of the Isothermal Formula. By LADISLAS NATANSON, Phys.D., Lecturer on Natural Philosophy, University of Cracow .....	301
XXXII. On a Permanent Magnetic Field. By W. HIBBERT, A.I.E.E., F.I.C. ....	307
XXXIII. Notices respecting New Books :—Mr. J. F. BLAKE's Annals of British Geology, 1890 .....	314
XXXIV. Intelligence and Miscellaneous Articles :— On the Refraction of Sound, and its Velocity in Porous Substances permeable to Sound, by N. HESSEHUS .....	316

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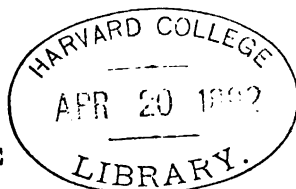
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XXXV. *On the Absorption-Spectra of some Copper Salts in Aqueous Solution.* By THOMAS EWAN, B.Sc., Ph.D., Dalton Scholar in Chemistry in the Owens College\*.

THE following research was undertaken in the hope of throwing some light on the question of the connexion between the absorption of light by salts in solution and their molecular structure.

On diluting a solution does a change in its absorption-spectrum take place? Whether this is so or not was the first point which I attempted to decide experimentally. A number of researches have already been carried out which bear on this question. The first of these is due to Beer †, who came to the conclusion that a change in the concentration of a solution has the same effect as a corresponding change in the thickness of the layer through which the light passes. The measurements of Bunsen and Roscoe ‡, and of Zöllner §, were in agreement with Beer's law. Melde ||, in 1865, found, by a qualitative method, that the law held good for dilute aqueous solutions of fuchsine; and the greater part of Vierordt's ¶ measurements also agree with it.

\* Communicated by the Author.

† Beer, Pogg. Ann. lxxvi. p. 78 (1852).

‡ Bunsen and Roscoe, Pogg. Ann. ci. p. 242 (1857).

§ Zöllner, Pogg. Ann. cix. p. 254 (1860).

|| Melde, Pogg. Ann. cxxvi. p. 284 (1865).

¶ Vierordt, *Die Anwendung des Spectralapparates*, etc., 1873; *Die Quantitative Spectralanalyse*, etc., 1876.

Lippich \*, in 1876, observed that the absorption-spectrum of didymium nitrate is different in strong and in dilute solutions. This was subsequently confirmed by H. Becquerel †.

In 1878 Glan ‡ made a careful series of measurements on aqueous solutions of several salts in different concentrations. He found differences between the absorptions of strong and dilute solutions of about the magnitude of the experimental error.

Settegast §, in 1879, found a small decrease in the absorption of solutions of potassium chromate and potassium bichromate, with increasing dilution. This was in agreement with the observations of Glan; while Vierordt (*loc. cit.*), Sabatier ||, and O. Knoblauch ¶ found a small increase in the absorption of the more dilute solutions.

O. Hesse \*\* (1880) examined alcoholic solutions of cyanine, and obtained numbers which did not agree with Beer's law. His experimental error appears to have been rather large, however; and more recently Ketteler and Pulfrich †† have shown that the law holds accurately for such solutions.

The measurements of Pulfrich †† and of Krüss §§ on potassium permanganate, and of Marshall ||| and C. Norden ¶¶ on carbonyl hæmoglobin and oxyhæmoglobin respectively, show that in these cases the extinction-coefficients are not strictly proportional to the concentrations.

The measurements of B. Walter \*\*\* on solutions of fluoresceïn in ammonia show that Beer's law only holds good up to a certain concentration, above which deviations occur.

Knoblauch †††, finally, was unable to observe any difference between the spectra of strong and dilute solutions of a number of salts which he examined; in a number of other cases differences were observed.

\* Lippich, *Wien. Akad. Anz.* 1876, p. 93.

† Becquerel, *Compt. Rend.* cii. p. 106 (1886).

‡ Glan, *Wied. Ann.* iii. p. 54 (1878).

§ Settegast, *Wied. Ann.* vii. p. 242 (1879).

|| Sabatier, *Compt. Rend.* ciii. p. 49 (1886).

¶ Knoblauch, *Wied. Ann.* xliii. p. 738 (1891).

\*\* Hesse, *Wied. Ann.* xi. p. 871 (1880).

†† Ketteler and Pulfrich, *Wied. Ann.* xv. p. 337 (1882).

†† Pulfrich, *Wied. Ann.* xiv. p. 177 (1881).

§§ Krüss, G. and H., *Kolorimetrie u. Quantitative Spectralanalyse*, p. 156 (1891).

||| J. Marshall, see Krüss, *loc. cit.* p. 211.

¶¶ C. Norden, see Krüss, *loc. cit.* p. 210.

\*\*\* B. Walter, *Wied. Ann.* xxxvi. p. 518 (1889).

††† Knoblauch, *Wied. Ann.* xliii. p. 738 (1891).



It would appear, therefore, that the absorption-spectrum of a substance in solution is, as a rule, variable to a greater or smaller extent with the concentration.

The second question which received attention was the connexion between the spectra of the salts of the same acid or base in aqueous solution.

Gladstone\*, in 1857, said that "a particular base or acid has the same effect on the rays of light, with whatever it may be combined in aqueous solution." This law, he found, held good generally though not invariably; and this conclusion was afterwards confirmed by the researches of Bahr and Bunsen†, Bunsen‡, Landauer§, Morton and Bolton||, Russel and Lapraik¶, Soret\*\*, Russel††, Knoblauch, and others.

A discussion of a number of these papers is to be found in a Report on Spectrum Analysis by Dr. Schuster in the British Association Reports, 1882. I will therefore content myself by referring to it. Morton and Bolton found that a large group of double acetates of uranium possess the same absorption-spectrum. Knoblauch found in one experiment that the bands of the nitrate and acetate of uranium occupied the same position in dilute solutions, while in stronger solutions they had different positions. The chloride and acetate had the same spectrum. Russel and Lapraik found that the nature of the acid had no influence on the spectrum of uranic salts; while Oeffinger (Dissertation quoted by Knoblauch) apparently found no two salts of uranium with the absorption-bands in exactly the same position. The discrepancies are perhaps due to the different observers using solutions of different concentrations.

Knoblauch has shown that, even in the most dilute solutions, the spectra of the copper and potassium salts of eosin are not identical.

The photometric researches bearing on this question are very few in number. The work of Settegast‡‡ and of Sabatier§§ shows that potassium and ammonium bichromates

\* Gladstone, Phil. Mag. (4) xiv. p. 418 (1857), and Journ. Chem. Soc. x. p. 79 (1858).

† Bahr and Bunsen, Liebig's Ann. cxxxvii. p. 20 (1866).

‡ Bunsen, Pogg. Ann. cxxviii. p. 100 (1866).

§ Landauer, Berliner Ber. xi. p. 1772 (1872).

|| Morton and Bolton, Chem. News, xxviii. p. 47 (1873).

¶ Russel and Lapraik, Nature, xxxiv. p. 510 (1886).

\*\* Soret, Compt. Rend. lxxvi. p. 708 (1878).

†† Russel, Proc. Roy. Soc. xxxii. p. 258 (1881).

‡‡ Settegast, Wied. Ann. vii. p. 242 (1879). { See also Ostwald, Zeit. Phys

§§ Sabatier, Compt. Rend. ciii. p. 49 (1886). { Chem. ii. p. 78 (1888).

and chromic acid have very nearly the same absorption-spectrum, while that of potassium chromate is quite different.

Erhardt\* found that the violet solutions of potassium and ammonium chrome-alums and of chromium sulphate have identical absorption-spectra, while that of chromic chloride is only very slightly different. The spectra of the other salts examined were considerably different.

As may be seen from the foregoing historical summary the experimental material is hardly sufficient to decide whether the absorptions of acid and base in aqueous solution are really independent or not. In strong solutions, speaking generally, they are not; but on dilution changes, greater or smaller, occur, and it is natural to inquire whether there is a limiting dilution beyond which no further change in the absorption occurs, and secondly, supposing that the limit exists, whether the acid and base will exercise their absorptions independently of each other in solutions more dilute than the limit.

To obtain answers to these questions, it was necessary to make photometric measurements of the fraction of the light of each wave-length absorbed by a molecule of different salts of the same metal in solutions of different concentrations. The salts of copper were used, as they seemed to form a suitable material for the measurements.

A preliminary set of measurements was made by a method not unlike that used by Knoblauch †, but I believe slightly more accurate, owing to the fact that it allows the spectra of the two solutions which are being compared to be seen simultaneously, side by side, in the spectroscope. A short description of it may therefore not be out of place.

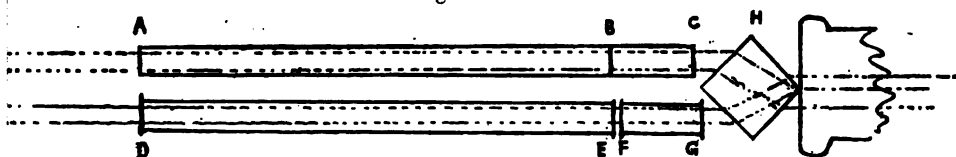
The spectroscope used was a one-prism graduated arc instrument, by Hilger. The prism had a dispersion from A to H of about  $6^{\circ} 20'$ . The solutions were contained in troughs in such a way that a long layer of a dilute solution could be compared with a short layer of a correspondingly strong one. The lengths of the layers and the concentrations of the solutions were always taken inversely proportional to each other; so that the light in both cases passed through the same amount of copper salt. In order that it should also pass through the same amount of water in each case, a long tube full of water was placed in front of the short tube con-

\* Erhardt, Inaugural Dissertation, Freiberg, 1875 ?

† These experiments were carried out in January and February 1891; that is, several months before Knoblauch's paper was published.

taining the concentrated solution. The diagram, fig. 1, will make the arrangement sufficiently clear.

Fig. 1.



A B C is a trough having a movable water-tight partition of glass at B. D E was the compensating-tube, full of distilled water; F G the tube destined to contain the concentrated solution. A B and D E were each 888 millim. long, and B C and F G each 102 millim. The light coming from a large Argand burner was rendered approximately parallel by means of a lens. The two bundles of light, after traversing the solutions, pass through the glass cube H, by which means the two spectra are seen, the one above the other, and only separated by a narrow black band due to the edge of the cube, which was not quite sharp. The experiments were carried out as follows:—The tubes B C and F G were filled with a strong solution of, say, copper sulphate, and the tubes A B and D E with distilled water. The volumes put into A B and B C were proportional to the lengths of the two parts. The lamp was then arranged so that the two spectra appeared equally bright, and as nearly as possible the same in every respect; measurements of both were then made. The movable partition at B was then removed, the solution in B C mixed with the water in A B, the partition replaced, and measurements made again of the spectrum. By this means any change due to dilution which occurred would be detected. The absorption of the copper salts examined consists of a strong general absorption in the red, and a greater or smaller absorption in the violet and blue. The readings were made by means of a vertical fibre of silk in the eyepiece of the observing-telescope. The positions of the extreme ends of the luminous spectrum were read, and also the positions in which the silk fibre was just visible against the luminous background of the spectrum. The spaces between these readings were taken as the penumbra. The measurements made on the divided arc of the spectroscope were reduced to wave-lengths by interpolation in a curve constructed from measurements of various known lines, which were repeated from time to time.

The following table contains the numbers obtained for copper chloride. Under  $\lambda_1$  are the wave-lengths of the two positions read for concentrated solutions; under  $\lambda_2$  the same readings for dilute solutions. The dilute solutions were about  $\frac{1}{10}$  the concentration of the strong solutions. The numbers are all the means of two or three readings, and the concentrations are given in gram-equivalents of salt in 1 litre of solution. The differences are taken so that a positive difference means an increase in the length of the visible spectrum, and *vice versa*.

TABLE I.—Copper Chloride.

Con- centration of strong solutions.	Violet end.			Red end.		
	$\lambda_1$ .	$\lambda_2$ .	$\lambda_1 - \lambda_2$ .	$\lambda_1$ .	$\lambda_2$ .	$\lambda_2 - \lambda_1$ .
4.261	478.7	429.6	+49.1	528.4	531.2	+2.8
	486.8	443.0	+43.8	543.2	540.8	-2.4
2.1305	451.0	439.0	+12.0	537.2	539.6	+2.4
	463.0	451.0	+12.0	551.6	552.4	+0.8
1.7044	431.0	427.6	+ 3.4	572.0	567.8	-4.2
	444.6	437.2	+ 7.4	576.4	579.4	+3.0
1.3612	426.2	421.0	+ 5.2	575.2	575.0	-0.2
	435.8	428.0	+ 7.8	579.8	577.4	-2.4
1.227	424.0	415.4	+ 8.6	580.6	580.6	$\pm 0$
	430.6	427.0	+ 3.6	584.0	584.0	$\pm 0$
1.018	414.8	412.4	+ 2.4	596.6	596.6	$\pm 0$
	420.8	417.8	+ 3.0	602.0	602.0	$\pm 0$

The temperature varied from 15° to 17°·2 on different days. The wave-length of the extreme violet end of the spectrum when the trough was filled with distilled water was found (on different days) 416.0, 417.2, and 411.2. This shows that the more dilute solutions transmitted the whole of the violet light. The average difference of a single reading from the mean was about  $\pm 1.5$  units in the wave-length.

The above numbers show that the position of the absorption at the red end of the spectrum does not vary with dilution. The differences vary irregularly in sign, and are of about the magnitude of the experimental error. The absorption in the violet (which extends into the green in the case of the strongest solution) disappears on dilution, so that a layer of 102 millim. of a solution containing about 1 gram-equivalent of salt in a litre shows no noticeable absorption. No change can, of course, be seen on further dilution; it would, however, be

rash to conclude that the change has reached a limit at a dilution of 1 gram-equivalent in a litre, as with an Argand burner the visible spectrum only extends to about halfway between G and H; it probably goes on till much greater dilutions are reached, only in the ultra-violet.

TABLE II.

CuSO <sub>4</sub> .						
Con- centration of strong solution.	Violet end.			Red end.		
	$\lambda_1$ .	$\lambda_2$ .	$\lambda_1 - \lambda_2$ .	$\lambda_1$ .	$\lambda_2$ .	$\lambda_2 - \lambda_1$ .
1.89	419.2	419.2	$\pm 0.0$	557.0	557.3	$+0.3$
	428.0	427.4	$+0.6$	568.4	568.4	$\pm 0.0$
Cu(NO <sub>3</sub> ) <sub>2</sub> .						
4.4323	429.0	429.7	$-0.7$	525.7	525.7	0.0
	440.2	438.3	$+1.9$	527.8	527.8	0.0

The concentration appears to have no influence on the spectra of copper sulphate and nitrate. This agrees with the results of Knoblauch; but, as will be seen later, this is not quite accurate, the concentration really exerting a small influence on the spectra.

Comparisons of the absorptions of CuCl<sub>2</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> in tolerably dilute solutions showed that no appreciable difference exists between them. The numbers obtained are given in Table III. (p. 324).

This method of merely comparing the limits of the spectra of two solutions does not appear to be sufficiently accurate. It is quite possible that general absorptions may exist in a spectrum which, not being sufficiently large to altogether extinguish the light at any place, may pass unnoticed. For example, the photometric measurements made on a strong solution of copper nitrate showed that it exerts a small general absorption over the violet part of the spectrum. This entirely escaped detection by the method described.

According to B. Walter\*, the width of the penumbra round an absorption-band is connected closely with the presence of

\* B. Walter, Wied. Ann. xxxvi. p. 523 (1889). Compare Böhlendorff, Wied. Ann. xliii. p. 784 (1891).

TABLE III.

Concentrations.		Length of layer.		Violet end.			Red end.		
$\text{Cu}(\text{NO}_3)_2$	$\text{CuCl}_2$	$\text{Cu}(\text{NO}_3)_2$	$\text{CuCl}_2$	$\lambda_1 \text{ CuCl}_2$	$\lambda_2 \text{ Cu}(\text{NO}_3)_2$	$\lambda_1 - \lambda_2$	$\lambda_1 (\text{CuCl}_2)$	$\lambda_2 \text{ Cu}(\text{NO}_3)_2$	$\lambda_2 - \lambda_1$
1.018	0.1048	102 mm.	990 mm.	413.6 417.6	409.7 414.0	+3.9 +3.6	597.6 603.7	597.6 603.7	$\pm 0.0$ $0.0$
0.814	0.814	102 "	102 "	413.6 —	413.8 —	-0.2 —	596.0 605.4	596.0 605.4	$\pm 0.0$ $0.0$
0.814	0.0838	102 "	990 "	412.1 —	412.8 —	-0.7 —	596.7 602.0	594.3 602.0	-2.4 $\pm 0.0$

TABLE IV.

Concentrations .....	4.261.	2.1305.	1.7044.	1.36.	1.23.	1.02.	0.44.	0.22.	0.176.	0.140.	0.126.	0.105.
Breadth at Red end.....	14.8	14.4	4.4	4.8	4.6	5.4	8.6	12.8	11.6	2.4	3.4	6.4
Breadth at Violet end.....	8.1	12.0	13.6	9.6	14.6	6.0	14.4	12.0	9.6	7.0	11.6	5.4

more complex molecular aggregates in the solution. On diluting a strong solution of copper chloride, he found a sudden change, at a certain point, in the width of the penumbra, due to the breaking-up of the complex molecules. Table IV. (p. 324) contains the measurements of the breadth of the penumbra, calculated from Table I., for a number of solutions of copper chloride.

On the whole the numbers cannot be regarded as showing any sudden diminution in the breadth of the penumbra. The variations appear to be accidental, and are probably due to variations in the brightness of the spectra caused by alterations in the relative positions of the lamp and the tubes containing the solutions.

### *Photometric Results.*

The method of Vierordt was employed, the instrument used being a universal spectro-photometer by A. Krüss of Hamburg. As this instrument has already been described elsewhere\*, no lengthy description of it will be necessary. The apparatus consists of an ordinary spectroscope, the slit of which is divided into two halves, each of which opens symmetrically, and in an accurately measurable manner, by means of micrometer-screws, the heads of which carry circles divided into 100 parts. By this means it is possible to vary the brightness of the upper and lower halves of the spectrum independently of each other by varying the width of the slits. A second slit in the eyepiece of the observing-telescope makes it possible to cut out a band in any part of the spectrum. The position of the centre and of the edges of this slit (which also opens symmetrically) can be read off by means of micrometer-screws.

The ocular slit was opened 56 divisions (on its screw), which corresponds to a breadth of about 0.27 millim. This divided the whole length of the visible spectrum into 19 parts, in each of which measurements were made.

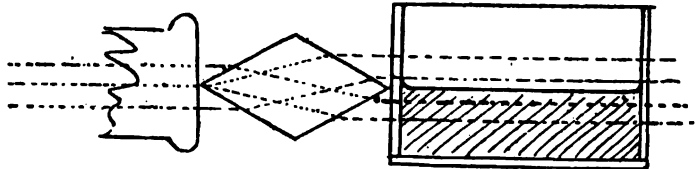
For an account of the precautions which must be taken in using the instrument it will be sufficient to refer to the works of G. and H. Krüss and of Vierordt, more especially *Die Anwendung des Spectralapparates zur Photometrie der Absorptions-spectren* (Tübingen, 1873).

The solutions were contained in cells of various lengths. As the measurements are most accurate when the absorption lies between 50 and 85 per cent. of the total light, the length

\* *Berichte*, xix. p. 2739 (1886); *Zeitschrift anal. Chem.* xxi. p. 182 (1882); G. & H. Krüss, *Kolorimetrie*, p. 90 *et seq.*

of layer was chosen so that the absorptions to be measured should as often as possible fall between these limits. Three cells were used—viz. a Schulz cell, the glass cube of which had a thickness of 1.006 centim., and two troughs, 7.64 and 22.86 centim. long respectively. When using these troughs the liquid only filled the lower half, the meniscus being placed at the level of the division between the two halves of the double slit. As, however, this produces a black band, about 2 millim. broad, between the two spectra, thereby greatly increasing the difficulty of comparing their brightness, a flint-glass rhomb was placed between the trough and the slit, in the same way as in Hüfner's spectro-photometer\*. The arrangement is shown in fig. 2.

Fig. 2.



The ends of the trough were provided with screens of blackened card of sufficient width to prevent reflexions from the sides of the trough or from the meniscus. The source of light was, as before, the Argand burner. The measurements were made in a dark room, and extraneous light shut off from the apparatus as much as possible by screens, and from the eye of the observer by a piece of black velvet which covered the eyepiece of the observing-telescope. The light from the Argand burner was concentrated by means of two lenses on a hole, about  $\frac{1}{16}$  inch diameter, in a black screen, and after passing this was made parallel by a lens of about 15 inches focal distance. The light thus obtained was rather faint, but it was not found possible to obtain reliable results otherwise. The salts examined were carefully purified and the solutions made with twice distilled water. They were filtered immediately before being examined through fine Swedish filter-paper. All the solutions were analysed after being filtered, as the filtration made a small difference in the concentration. The analyses were made by the very convenient method—titration, with thiosulphate solution, after adding excess of potassium iodide—described by Westmoreland†. The con-

\* *Zeit. Phys. Chem.* iii. p. 562 (1889).

† *Journ. Soc. Chem. Ind.* 1886, p. 48.



centrations are, as before, given in gram equivalents in one litre of solution.

The measurements are made as follows :—The cell, either empty or filled with distilled water, is adjusted before the slit of the spectroscope on a suitable stand, and the ratio of the intensities of the light which has passed through the upper and lower halves of the trough is read, in various parts of the spectrum. This gives the correction to be applied on account of the apparatus. The solution is now placed in the trough, and readings made through as much of the spectrum as possible. Ten or more single readings were made in each region and the mean taken.

The formulæ which I have used in reducing the results are:—(1) For the Schulz cell,

$$(1-p) = \frac{b(1-\beta''')^2}{(1-\beta')^2 \cdot a}$$

(2) For the ordinary troughs,

$$(1-p) = \frac{b(1-\beta)^2}{(1-\beta'')^2(1-p') \cdot a};$$

where

$a = \frac{\text{width of lower slit}}{\text{width of upper slit}}$ , the two spectra having been made of equal brightness, and the empty trough being before the slit.

$b$  is the same ratio when the trough contains the solution.

$p$  the fraction of the incident light absorbed by the dissolved substance.

$p'$  = the fraction absorbed by the water.

$\beta$  = loss by reflexion at surface between ends of trough and air.

$\beta'$  = loss by reflexion at surface between Schulz cube and air.

$\beta''$  = loss by reflexion at surface between ends of trough and solution.

$\beta'''$  = loss by reflexion at surface between Schulz cube and solution.

The loss of light due to the absorption of the water was calculated from the numbers of Hüfner and Albrecht\*. The following table contains the numbers which were used in reducing the results.

\* Wied. *Ann.* xlii. p. 1 (1891).

TABLE V.

Region in Spectrum.	$\epsilon$ .	(1-p') for 7.64 centim.	(1-p') for 22.87 centim.
$\lambda$ 627.7— $\lambda$ 599.4	0.00108	0.981	.....
599.4—574.2	0.00073	0.987	.....
574.2—551.6	0.00039	0.993	0.980
551.6—534.1	0.00028	0.996	0.986
534.1—518.2	0.00019	0.997	0.990
518.2—502.3	0.00018	0.997	0.990
502.3—488.3	0.00017	0.998	0.991
488.3—474.6	0.00016	.....	0.992
474.6—462.8	0.00015	.....	0.993

The quantity  $(1-p)$  is the fraction of the incident light which has escaped being absorbed by the dissolved substance, and is dependent on the length of layer and concentration of solution. In order to obtain comparable numbers, the extinction-coefficients and absorption-ratios have been calculated from the values of  $(1-p)$ . A few words on the connexion of these quantities with one another are perhaps not altogether superfluous.

According to Lambert's law we have

$$I' = I\alpha^n, \quad \dots \dots \dots (1)$$

where  $I'$  is the light transmitted by a layer of thickness  $n$ , of a substance the coefficient of transmission of which is  $\alpha$ .  $I$  is the original intensity of the light.

Bunsen and Roscoe\* define the extinction-coefficient as the reciprocal of that length of layer of a solution which will reduce the intensity of light by absorption to  $\frac{1}{10}$  of its original value.

Substituting, therefore, in equation (1),  $I' = \frac{1}{10}$ ,  $I = 1$ , and

$$n = \frac{1}{\epsilon}, \text{ we get } \frac{1}{10} = \alpha^{\frac{1}{\epsilon}},$$

$$\text{or } \epsilon = -\log \alpha. \quad \dots \dots \dots (2)$$

From equation (1) we have also

$$-n \log \alpha = \log I - \log I'.$$

Substituting the value of  $-\log \alpha$  and putting  $I = 1$ , we get

$$\epsilon = -\frac{\log I'}{n}.$$

$I'$  is the quantity which before has been called  $(1-p)$ .

\* Pogg. Ann. ci. p. 235 (1857).

Further, according to Beer's law, if there are two solutions of the same substance, of concentrations  $c$  and  $c'$ , and in lengths of layer  $l$  and  $l'$ , such that

$$cl = c'l', \quad \dots \dots \dots (1)$$

they will absorb the same fraction of the light which passes through them.

Suppose they both transmit the fraction  $I'$ , then

$$\epsilon = -\frac{\log I'}{l} \quad \text{and} \quad \epsilon' = -\frac{\log I'}{l'}, \quad \dots \dots (2)$$

$\epsilon$  and  $\epsilon'$  being the extinction-coefficients of the two solutions. From (1) we find

$$-\frac{cl}{\log I'} = -\frac{c'l'}{\log I'}; \quad \dots \dots \dots (3)$$

and from (2) and (3), finally, we have

$$\frac{c}{\epsilon} = \frac{c'}{\epsilon'}.$$

That is, the concentration is proportional to the extinction-coefficient, and  $\frac{c}{\epsilon} = A$ .  $A$  is, if Beer's law is true, a constant only dependent on the wave-length of the light and on the nature of the substance. The quantity  $A$  is called by Vierordt the absorption-ratio (*Absorptions-verhältnisse*).

The following example will make the method of reducing the results clear:—

Solution of  $\text{CuCl}_2$ , concentration = 2.113 gr. eq. in 1 litre.  
Trough 7.64 centim. long.

The apparatus-correction  $a$  was found 1.003, as a mean of 25 readings in various positions in the spectrum.

The following readings were taken with the solution in the trough, in the region between  $\lambda 518.2$  and  $\lambda 502.3$ .

Breadth of upper slit.	Lower slit Upper slit ( $b$ )	Number of Readings.	Greatest difference between two Readings.	Mean ( $b$ ).
140	.484	5	3.8	0.485
100	.487	5	2.3	

The refractive index of the ends of the trough was 1.526.

“ “ of the solution was . . . 1.362.

$\beta$  and  $\beta''$  are calculated by Fresnel's formula— $\left(\frac{n-1}{n+1}\right)^2$ , which gives  $\beta=0.0433$  and  $\beta''=0.00325$ . The fraction of light transmitted by 7.64 centim. of water is taken from Table V. Putting these values into the expression given for the ordinary troughs, we get

$$(1-p) = \frac{0.485 \times (1-0.0433)^2}{(1-0.00325)^2 \times 0.997 \times 1.003} \\ = 0.4473.$$

As  $\epsilon = -\frac{\log(1-p)}{l},$

where  $l$  = length of layer,

$$l\epsilon = -\log(1-p) \\ = 0.34944.$$

Again,  $A = \frac{c}{\epsilon} = \frac{cl}{\epsilon l};$

$$\log A = \log c + \log l - \log \epsilon l \\ = \log(2.113) + \log(7.64) - \log(0.34944);$$

$c$  = concentration in gram equivalents in 1 litre of solution.

On calculating out the above expression,

$$A = 46.2.$$

#### Probable Error.

As there is no reason why the error should be greater in one set of measurements than in another (the measurements being all of the same kind), I have only calculated it for one set of numbers, obtained with a solution of copper chloride containing 2.113 equiv. in 1 litre. The probable error was calculated by the formula  $\pm 0.6745 \sqrt{\frac{S}{n(n-1)}}$ . The results are contained in Table VI.

TABLE VI.

Region in Spectrum.	Number of Readings.	(1-p).	Y.	Z.
551.6—534.1	15	0.083	$\pm 0.0014$	$\pm 3.5$
534.1—518.2	15	0.2599	.0016	1.3
518.2—502.3	10	0.4855	.00289	1.3
502.3—488.3	15	0.7020	.00371	1.1
488.3—474.6	15	0.7972	.00469	1.3
474.6—462.8	10	0.7676	.00616	1.7
462.8—452.2	10	0.6125	.00410	1.5
452.2—443.1	10	0.3893	.00376	3.5
443.1—434.2	5	0.1890	.00334	3.7

The final value of  $(1-p)$  is calculated from two photometric measurements of the same kind; one, the correction for the apparatus, the other the measurement of the light which passes through the solution. These will both be subject to an error of the magnitude given in column Y. The probable error of the final result will therefore be double this amount. The numbers in column Z represent this final error, calculated as percentages of  $(1-p)$ . The large error in the violet is due to the small intensity of the light used in that part of the spectrum, and also to the fact that the eye is less sensitive to differences in the intensity of light in the violet than in the middle of the spectrum. At the red end of the spectrum a special error makes itself felt. The measurements are only theoretically accurate, when the part of the curve representing the intensity of the light in the part of the spectrum in which they are made may be considered as a horizontal line. When the absorption-curve of the substance under examination rises or falls rapidly this is no longer the case, and for this reason the measurements on the copper salts in the red end of the spectrum are less accurate than in other parts.

My first measurements on the absorptions by copper sulphate showed a lack of agreement between the numbers obtained with the same solution when different lengths of layer were used. This was found to be due to the light not being parallel, as the differences disappeared when parallel light was used. Something similar appears to have been observed by other investigators. Vierordt\* found (with a lamp 15 centim. from the slit, and distilled water in the trough) the ratio of the intensity of the light which had passed through the empty half of the trough to that which had passed through the water to be 0.8; the calculated number is 0.936. Krüss† found the ratio in a Schulz cell 0.905, that calculated being 0.993. I also found the ratio in a Schulz cell 0.91, when the light was not parallel.

The cause of these differences may be found in the fact that placing a layer of a medium with a greater refractive index than air in the path of the light has the same effect as bringing the light nearer to the slit through a distance which is given by the formula  $l\left(\frac{\mu-1}{\mu}\right)$ , where  $l$  is the thickness of the layer of the medium, and  $\mu$  its refractive index. It must also be remembered that, so long as the collimator is filled with light, an alteration in the distance of the lamp makes no difference in the intensity of the light in the spectrum. The

\* *Anwendung* &c. pp. 5 and 24.

† *Kolorimetrie*, p. 153.

distance of the lamp must therefore be measured from the point at which the collimator just ceases to be filled with light. A comparison with a set of measurements made with pure water showed that at least a considerable part of the difference observed is to be explained in this way.

The following Tables contain a number of measurements which were made with parallel light and distilled water in the troughs. The good agreement found between the calculated and observed numbers shows that the loss of light due to dust in the liquids cannot have been very great.  $I$  is the ratio of the intensities of the light after passing through the upper and lower halves of the trough.

TABLE VII.

Region in Spectrum.	$I$ (found).	$I$ (calculated).	Difference.
Schulz Cell.			
$\lambda$ 599.4— $\lambda$ 574.2	0.985	0.987	+0.002
551.6—534.1	0.991	0.985	-0.006
Schulz Cell.			
$\lambda$ 627.7— $\lambda$ 599.4	0.983	0.987	+0.004
599.4—574.2	0.979	0.987	+0.008
574.2—551.6	0.982	0.986	+0.004
551.6—534.1	0.985	0.985	$\pm 0.000$
518.2—502.3	0.988	0.985	-0.003
Layer of water, 7.64 centim.			
$\lambda$ 627.7— $\lambda$ 599.4	0.949	0.941	-0.008
599.4—574.2	0.939	0.935	-0.004
574.2—551.6	0.948	0.929	-0.019
551.6—534.1	0.935	0.927	-0.008
534.1—518.2	0.926	0.926	$\pm 0.000$
502.3—488.3	0.909	0.926	+0.017
488.3—474.6	0.919	0.926	+0.007
Layer of water, 22.87 centim.			
$\lambda$ 534.1— $\lambda$ 518.2	0.927	0.934	+0.007
502.3—488.3	0.925	0.933	+0.008
474.6—462.8	0.917	0.931	+0.014

The effect of dust would be to make the observed numbers higher than those calculated. This is sometimes the case, sometimes the reverse.

Table VIII. contains the details of the measurements made on the solutions of copper salts.

Under *c* are found the concentrations of the solutions, in gram equivalents of salt in 1 litre of solution; under *l* the length of layer in centim.; *ε* is the extinction-coefficient, and *A* the absorption-ratio.

TABLE VIII.

Copper Sulphate.					
<i>c.</i>	<i>l.</i>	Region in Spectrum.	(1- <i>p</i> ).	<i>l. ε.</i>	<i>A.</i>
2.0324	1.006	λ. λ.			
		627.7-599.4	0.083	1.08096	1.89
		599.4-574.2	0.2944	0.53102	3.85
		574.2-551.6	0.4930	0.30714	6.66
		551.6-534.1	0.6985	0.15582	13.12
2.0324	7.64	534.1-518.2	0.8171	0.08774	23.25
		518.2-502.3	0.0611	1.21424	12.79
		502.3-488.3	0.2220	0.65357	23.76
		488.3-474.6	0.4454	0.35130	44.20
		474.6-462.8	0.6716	0.17286	89.8
2.3808	22.87	462.8-452.2	0.0697	1.15643	47.07
		452.2-443.1	0.2490	0.60386	90.15
		443.1-434.2	0.5021	0.29925	181.9
		434.2-427.0	0.6734	0.17176	316.9
		427.0-414.2	0.7723	0.11220	485.2
0.2856	7.64	414.2-402.3	0.8103	0.09137	595.8
		402.3-390.4	0.7873	0.10384	523.0
		390.4-374.2	0.7846	0.10535	516.7
		374.2-351.6	0.0614	1.21468	1.796
		351.6-334.1	0.2290	0.64017	3.408
0.2842	22.87	334.1-318.2	0.4700	0.32791	6.654
		318.2-302.3	0.6880	0.16242	13.43
		302.3-288.3	0.1077	0.96793	6.715
		288.3-274.6	0.2930	0.53305	12.19
		274.6-262.8	0.5066	0.29361	22.14
		262.8-252.2	0.6884	0.16216	40.08
		252.2-243.1	0.8377	0.07690	84.52
		243.1-234.2			
		234.2-227.0			
		227.0-220.0			
Copper Chloride.					
4.211	1.006	599.4-574.2	0.0799	1.09711	3.86
		574.2-551.6	0.2403	0.61918	6.84
		551.6-534.1	0.4971	0.30355	13.95
		534.1-518.2	0.6987	0.15573	27.20
		518.2-502.3	0.8339	0.07888	53.70
		502.3-488.3	0.8764	0.05731	73.92
		488.3-474.6	0.7981	0.09797	43.24
		474.6-462.8	0.6591	0.18109	23.39
		462.8-452.2	0.4131	0.38395	11.03
		452.2-443.1	0.2104	0.67687	6.26

Table VIII. (continued.)

Copper Chloride (continued).					
c.	l.	Region in Spectrum.	(1-p).	l. e.	A.
2.113	1.006	$\lambda.$			
		$\lambda.$			
		627.7-599.4	0.0787	1.10406	1.92
		599.4-574.2	0.2536	0.59594	3.57
		574.2-551.6	0.4832	0.31587	6.73
2.113	7.64	551.6-534.1	0.6854	0.16405	12.96
		534.1-518.2	0.8187	0.08687	24.47
		434.2-427.0	0.7064	0.15091	14.09
		551.6-534.1	0.0765	1.11612	14.46
		534.1-518.2	0.2394	0.62092	26.00
		518.2-502.3	0.4473	0.34944	46.20
		502.3-488.3	0.6467	0.18929	85.26
		488.3-474.6	0.7344	0.13406	120.4
		474.6-462.8	0.7064	0.15093	107.0
		462.8-452.2	0.5637	0.24896	64.99
2.117	1.006	452.2-443.1	0.3583	0.44579	36.20
		443.1-434.2	0.1739	0.75961	21.25
		627.7-599.4	0.0662	1.17904	1.81
		599.4-574.2	0.2495	0.60289	3.53
		574.2-551.6	0.4772	0.32131	6.63
0.4189	7.64	551.6-534.1	0.6796	0.16775	12.70
		434.2-427.0	0.7029	0.15313	13.91
		627.7-599.4	0.0216	1.66493	1.92
		599.4-574.2	0.1395	0.85558	3.74
		574.2-551.6	0.3428	0.46496	6.88
0.4189	22.87	551.6-534.1	0.5665	0.24678	12.97
		534.1-518.2	0.1931	0.71418	13.41
		518.2-502.3	0.3996	0.39833	23.99
		502.3-488.3	0.5962	0.22460	42.69
		488.3-474.6	0.7533	0.12303	77.87
			0.8495	0.07084	135.2

Copper Nitrate.					
4.51	1.00	574.2-551.6	0.159	0.79398	5.68*
3.9916	7.64	551.6-534.1	0.401	0.39449	11.46*
		534.1-518.2	0.04011	1.39671	21.83
		518.2-502.3	0.1560	0.80675	37.80
		502.3-488.3	0.3535	0.45165	67.52
		488.3-474.6	0.5184	0.28532	106.9
		474.6-462.8	0.6373	0.19569	155.8
		462.8-452.2	0.6591	0.18106	168.4
		452.2-443.1	0.6782	0.16867	180.8
		443.1-434.2	0.6458	0.18992	160.6
		434.2-427.0	0.6125	0.21289	143.2
		627.7-599.4	0.0415	1.38174	1.96
		599.4-574.2	0.1907	0.71958	3.77
		574.2-551.6	0.3588	0.44515	6.09
		551.6-534.1	0.5824	0.23480	11.55
0.3552	22.87	534.1-518.2	0.2218	0.65406	12.42
		518.2-502.3	0.3616	0.34477	23.56
		502.3-488.3	0.6669	0.17593	46.17
			0.8208	0.08576	92.57

\* These numbers were obtained with light which was not parallel.



The refractive indices of the solutions were determined for sodium light as follows:—

Substance.	Concentration.	Refractive Index.
CuSO <sub>4</sub> .....	2·1	1·365
" .....	0·28	1·336
CuCl <sub>2</sub> .....	4·2	1·388
" .....	2·1	1·362

Table IX. contains the absorption-ratios of all the solutions examined. The absorption-ratio for any substance in solutions of different concentration can be regarded as constant when the differences of concentration are small. The mean, therefore, of the numbers obtained with the solutions of nearly the same concentration has been taken.

TABLE IX.

Position in Spectrum.	CuSO <sub>4</sub> .		CuCl <sub>2</sub> .			Cu(NO <sub>3</sub> ) <sub>2</sub> .	
	2 eq.	0·28 eq.	4 eq.	2 eq.	0·4 eq.	4 eq.	0·35 eq.
λ. λ.							
627·7—599·4	1·89	1·79	.....	1·86	1·92	.....	1·96
599·4—574·2	3·85	3·41	3·86	3·55	3·74	.....	3·77
574·2—551·6	6·66	6·81	6·84	6·68	6·88	5·68	6·09
551·6—534·1	12·95	12·65	13·95	13·41	13·19	11·46	11·99
534·1—518·2	23·51	22·05	27·20	25·23	23·99	21·83	23·56
518·2—502·3	45·63	40·45	53·70	46·20	42·69	37·80	46·17
502·3—488·3	89·97	82·73	73·92	85·26	77·87	67·52	92·57
488·3—474·6	181·9	143·2	43·24	120·4	135·2	106·9	.....
474·6—462·8	316·9	.....	23·39	107·0	.....	155·8	.....
462·8—452·2	485·2	.....	11·03	64·99	.....	168·4	.....
452·2—443·1	595·8	.....	6·26	36·20	.....	180·8	.....
443·1—434·2	523·0	.....	.....	21·25	.....	160·6	.....
434·2—427·0	516·7	.....	.....	14·00	.....	143·2	.....

The absorption-spectrum of copper sulphate has already been measured by Glan\*. He has given his results in the form of fractions of light transmitted—(the quantity which I have called (1—p). The light, in Glan's experiments, passed vertically upwards through a glass trough, in the lower part of which was a layer of strong copper sulphate solution, and floating upon this a layer of distilled water. The fraction of the light transmitted was measured, the water and solution mixed together, and the measurement repeated. In order to compare my numbers with those of Glan I have calculated

\* Glan, Wied. *Ann.* iii. p. 54 (1878).

from the measurements on the strong solutions the part of the light which would be left after passing through a layer of 1 centim. thickness of a solution containing 2 gram equivs. of  $\text{CuSO}_4$  in 1 litre, and from the dilute solutions, the fraction which would remain after passing through 8 centim. of a solution containing 0.25 equivs. The results of the calculation are contained in the following Table :—

TABLE X.

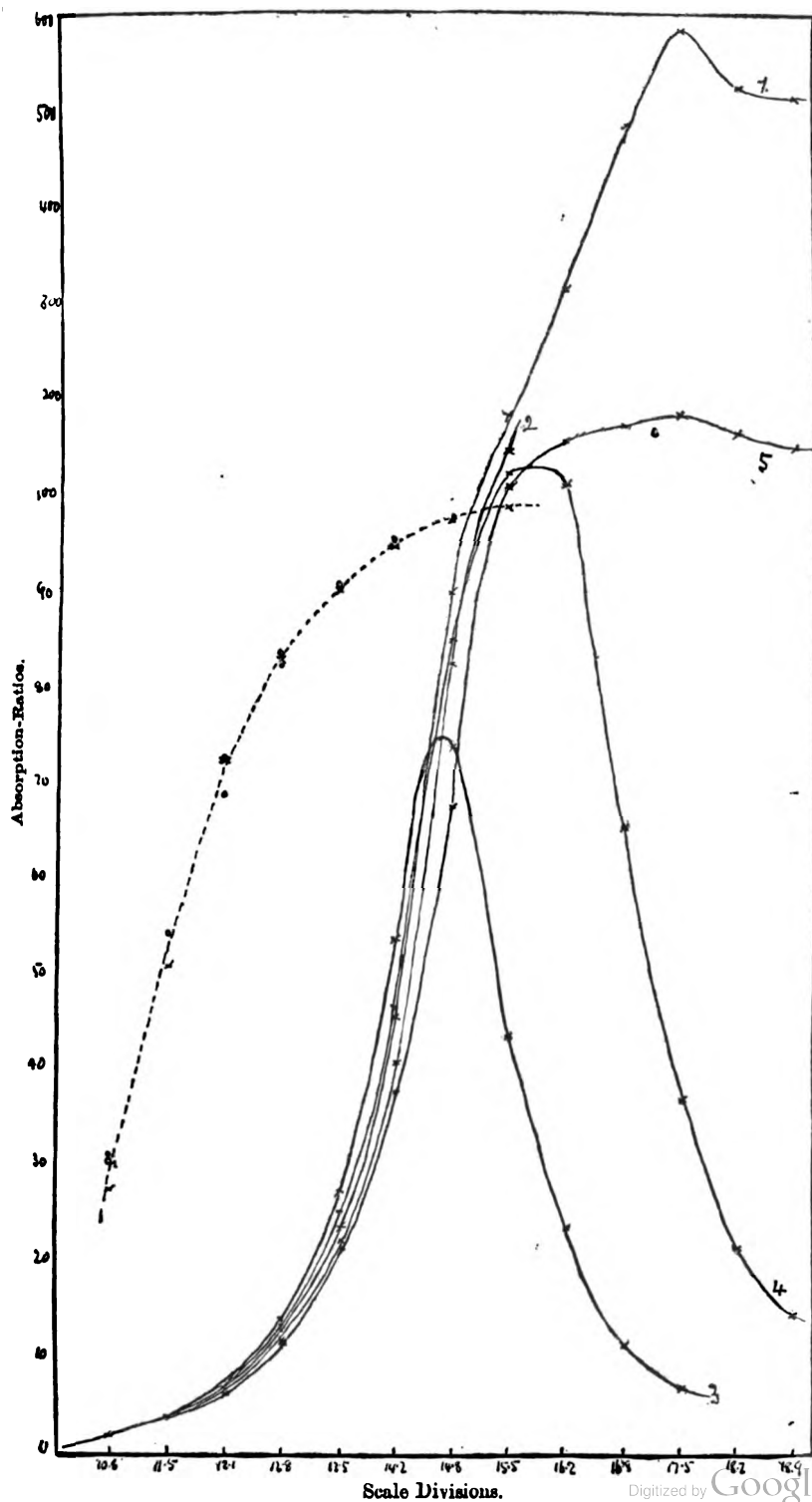
Region in Spectrum (mean $\lambda$ ).	(1-p) Conc. Solution.	(1-p) Dil. Solution.	Difference.
612.6	0.078	0.077	+0.001
586.1	0.302	0.259	+0.043
563.6	0.501	0.509	-0.008
543.3	0.701	0.695	+0.006
526.1	0.822	0.811	+0.011
509.7	0.904	0.892	+0.012
493.5	0.950	0.946	+0.004
481.5	0.975	0.968	+0.007

Glan's numbers are given for comparison in the following Table :—

TABLE XI.

Mean $\lambda$ .	(1-p) conc.	(1-p) dil.	Difference.	Dilution.
674	0.077	0.073	+0.004	1/7
659	0.155	0.150	+0.005	1/7
626	0.336	0.330	+0.006	1/5
{ 557	0.449	0.441	+0.008	1/3
{ 557	0.510	0.507	+0.003	1/7
{ 525	0.822	0.813	+0.009	1/3
{ 525	0.848	0.854	-0.006	1/7

With the exception of one number in each set of experiments, the differences are all in the same direction. They are, it is true, about the same magnitude as the experimental error, but the circumstance that the two sets of numbers were obtained by different methods and with different instruments seems to point to the existence of a real difference between the absorption of the strong and dilute solutions of  $\text{CuSO}_4$ . It is not, unfortunately, possible to compare the absolute magnitudes of the absorption, as Glan has only given the relative concentrations of his solutions (last column Table XI.). Glan's strongest solutions were, however, evidently saturated,



or nearly so, and his experiments are therefore comparable with mine.

The changes in the absorption-spectra of the solutions which occur when the concentration is changed are very clearly visible in the curves which represent the absorption-ratios. These are drawn for convenience with the divisions of the tangent-screw as abscissæ (instead of wave-lengths), and the values of the absorption-ratios as ordinates. Curves 1 and 2 belong to the strong and dilute solutions of copper sulphate, 3 and 4 represent the absorption-ratios of the copper-chloride solutions containing about 4 and 2 equivalents in 1 litre, and 5 belongs to  $\text{Cu}(\text{NO}_3)_2$ . The curves of the most dilute solutions of the three salts lie very close together and are almost identical with No. 2. The great similarity of the absorptions of these three solutions is best seen, not by comparing their absorption-ratios, but by comparing the fractions of the light transmitted by them, calculated for solutions containing the same amount of copper, and for unit length of layer. The comparison is carried out in Table XII. Comparing the absorptions in this way, it is possible to see whether the differences between them are greater than the experimental error or not. This is very difficult when the numbers are calculated as absorption-ratios, as the errors in the measurements are much exaggerated in parts of the spectrum where the absorption is small, and *vice versa*.

TABLE XII.\*

Region in Spectrum.	$\text{CuSO}_4$ .	$\text{CuCl}_2$ .	$\text{CuSO}_4$ — $\text{CuCl}_2$ .	$(\text{CuNO}_3)_2$ .	$\text{CuCl}_2$ — $\text{Cu}(\text{NO}_3)_2$ .
627.7—599.4	0.2775	0.3018	—0.0243	0.3096	—0.0078
599.4—574.2	0.5089	0.5403	—0.0314	0.5430	—0.0027
574.2—551.6	0.7130	0.7157	—0.0027	0.6854	+0.0303
551.6—534.1	0.8333	0.8398	—0.0065	0.8254	+0.0144
534.1—518.2	0.9008	0.9087	—0.0079	0.9069	+0.0018
518.2—502.3	0.9447	0.9474	—0.0027	0.9513	—0.0039
502.3—488.3	0.9725	0.9709	+0.0016	0.9759	—0.0050
488.3—474.6	0.9840	0.9831	+0.0009		

The numbers for copper chloride and copper nitrate are very similar, the differences are scarcely larger than the experimental error and vary in sign. The differences between copper sulphate and copper chloride, on the other hand, are nearly all in the same direction and sometimes considerably exceed the error of experiment.

\* The numbers are calculated for solutions containing 1 equivalent in 1 litre.

## CONCLUSIONS.

It is at once noticeable that the curves representing the absorption-ratios of all the solutions appear to start out from the same point at the red end of the spectrum and for a short distance to follow an identical course, diverging more and more widely as the wave-length decreases. It appears natural to attribute this absorption in the red, which is common to all the solutions, to the common constituent copper, and to attribute the differences partly to the absorption exercised by the acid radical itself, and partly to the influence which it has on the vibrations of the copper. Something analogous to this influence of the acid radical on the absorption of the copper was observed by Abney and Festing\* in their work on the absorption-spectra of organic and other compounds in the infra-red. They found that a number of definite lines in these spectra undoubtedly were due to hydrogen, but that the number of them and their relative intensity in any spectrum were dependent on the other atoms with which the hydrogen was combined. The investigations of Hartley, Krüss, Vogel, and others on the absorption-spectra of organic compounds have shown that the absorption of light by a substance is dependent on its chemical constitution. Every change in the nature, number, or linking of the atoms causes a corresponding change in the absorption-spectrum. So that in general when two substances are chemically combined the absorption-spectrum of the compound will be different from that of the constituents. On the other hand, when two substances which are not chemically united exist together in a solution, the absorption-spectrum is the sum of the two separate spectra. Arguing backwards, it seems probable that, if two substances in a solution absorb light independently of one another, so that replacing one of them by something else makes no difference in the absorption-spectrum of the other, then they are not chemically combined. In the dilute solutions of the three copper salts examined this appears to be—at least very nearly—the case. Replacing  $\text{SO}_4$  by  $\text{Cl}_2$  or by  $(\text{NO}_3)_2$  makes very little difference in the absorption, though in the strong solutions the difference made by such a replacement is very large. One would, therefore, seem to be forced to the conclusion that only in the strong solutions is the copper really chemically combined with the acid part of the salt, and that as the solutions become more and more dilute the dissociation of the salt becomes greater and greater. It has already been pointed out at the beginning of this paper that

\* Phil. Trans. (1881), Part III. p. 887.

in general salts in aqueous solution behave in the same way as these copper salts, though exceptions are known.

It only remains to compare briefly the results thus arrived at with existing theories of solution.

(1) According to the theory of Arrhenius the electrolytic dissociation in the most dilute copper solutions which were examined is by no means complete, and therefore the absorption-spectra of the three solutions should not be identical.

The degree of dissociation is calculated from the numbers of Kohlrausch\* for copper sulphate, of J. Trötsch† and J. H. van t'Hoff and Reicher‡ for copper chloride, and of Long§ for copper nitrate. The numbers obtained are as follows:—

CuSO <sub>4</sub> ,	0.2856 eq. in 1 l., $\mu=344$ , $\mu_{\infty}=1086$ ,	dissociation=31.7 per cent.
„	2.38 eq. in 1 l., $\mu=166$ „	=15.3 „
CuCl <sub>2</sub> ,	0.4189 eq. in 1 l., $\mu=64$ , $\mu_{\infty}=101$ ,	dissociation=63.4 „
Cu(NO <sub>3</sub> ) <sub>2</sub> ,	0.3552 eq. in 1 l., $\mu=65.8$ , $\mu_{\infty}=100?$ ,	dissociation=65.8 „

It is interesting to observe that the solutions of chloride and nitrate of copper in which the dissociation is far advanced and nearly to the same extent, possess almost identical absorption-spectra, whereas that of copper sulphate is noticeably different, which fact is in agreement with the theory, the dissociation in the copper-sulphate solution being very much less advanced than in the others.

It is as well to draw attention to the fact that before one can determine whether the limit of dilution after which the absorption no longer changes is identical with the limit at which the dissociation is complete, it may be necessary to examine the absorption in the ultra-violet and perhaps in the infra-red. The experiments in the first part of this paper with copper chloride seem to show that changes go on in the invisible violet after they have ceased in the visible part of the spectrum.

(2) Knoblauch has explained the alterations in the spectra of certain salts by assuming a hydrolytic dissociation in the more dilute solutions. In the case of copper salts there appears to be no reason for assuming that such a dissociation takes place to any extent. A hydrolytic dissociation of a

\* Wied. *Ann.* vi. p. 1 (1879); *ibid.* xxvi. p. 188 (1885).

† Wied. *Ann.* xli. p. 259 (1890).

‡ *Zeitschrift. Phys. Chem.* iii. p. 198 (1889).

§ Wied. *Ann.* xi. p. 37 (1880).

copper salt would lead (as it does with chromium salts) to a separation of hydroxide. The small amount of precipitate which forms in solutions of cupric salts after standing for some time appears to be due to impurities in the water (chiefly ammonia and carbon dioxide).

(3) According to the theory of Armstrong\* and Traube†, the changes in the absorption-spectra which occur on passing from concentrated to dilute solutions are due to the larger aggregates of molecules which exist in the concentrated solutions breaking up into smaller molecules. According to this theory, the molecules of the salt, even in the most dilute solutions, still exist as such; and these dilute solutions might therefore be expected to show characteristic differences, similar to those observed in the strong solutions. This at any rate in the case of cupric salts is not the case in the visible part of the spectrum.

(4) The changes of colour which the solutions of copper chloride exhibit when its solution is diluted have long been regarded as due to the formation of different hydrates. If we admit with Pickering the existence of hydrates in dilute solutions containing 1000 or more molecules of water, it is conceivable that two salts of the same metal with colourless acids should have in dilute solution the same spectrum, for the influence exercised on the vibrations of the metal by the acid radical would become negligible compared with that exercised by the 1000 water molecules. Two compounds such as  $\text{CuCl}_2 + 1000\text{H}_2\text{O}$  and  $\text{CuSO}_4 + 1000\text{H}_2\text{O}$  might well have the same spectrum. The experiments are hardly complete enough to allow of any very definite conclusion on this point, but as I am occupied with further experiments on the absorption-spectra I hope to return to it on another occasion.

The large changes of colour which often occur on diluting the solutions of the halogen salts of heavy metals may perhaps be connected not with hydrates but with the halogen. Gladstone‡ has pointed out that the spectra of strong solutions of the bromides of platinum, gold, copper, and of potassium palladium bromide, all appear to be made up of the absorptions of bromine-water and of a salt of the metal with a colourless acid. It appears as though the halogen when combined with a metal exercised its absorption in the same way as in the free state, but modified to a greater or smaller extent by the metal with which it is combined.

The following is a summary of the results arrived at :—

\* J. Chem. Soc. liii. p. 116 (1888).

† *Berichte*, xxiii. p. 3582 (1890).

‡ Gladstone, *Phil. Mag.* [4] xiv. p. 418 (1857).

(1) The absorption-spectra of the three salts examined undergo changes on diluting their solutions.

(2) These changes are of such a nature that the spectra tend to become identical in dilute solutions.

(3) The results of other observers show on the whole that salts of other metals behave in a similar way.

(4) The behaviour of the salts examined leads to the conclusion that, in strong solutions, the acid and basic parts of the salts are associated in producing absorption of light, while in dilute solutions they act independently in doing so.

(5) These results are in substantial agreement with the hypothesis of electrolytic dissociation.

(6) The results cannot be satisfactorily explained on the hypothesis of a hydrolytic dissociation, or on that of molecular aggregates.

In conclusion, I take this opportunity of expressing my thanks to Professor H. B. Dixon, at whose suggestion this investigation was begun, and also to Professor A. Schuster for the kindness with which he placed the Vierordt spectrophotometer and other apparatus at my disposal, and for much valuable advice in carrying out the work.

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#### XXXVI. *On Chemical Equilibrium in Mixed Electrolytes.*

*By* Dr. G. GORE, *F.R.S.\**

IN various researches I have shown that any change occurring in the molecular or chemical constitution of an electrolyte may be easily and quickly detected, and its amount and rate to a certain extent measured, either by the voltaic balance method, or by the simple plan of immersing a suitable voltaic pair of metals in the liquid successively at different periods of time, and noting either the degree of voltaic energy, electromotive force, or strength of current produced; and I have shown that in certain cases, the mixture of electrolytes, especially that of an aqueous solution of a halogen with one of a salt or base (and in some cases a very dilute solution of an acid with one of a salt), the liquid mixture does not at once attain its final or fixed state at 16° C., but attains it rapidly on the application of heat. (See "Method of Examining Rate of Chemical Change in Aqueous Solutions," *Proc. Roy. Soc.* March 14, 1890, p. 440. "On the Molecular Constitution of Isomeric Solutions," *Phil. Mag.* Oct. 1889, p. 289. "Method of Measuring Loss of Energy due to Chemical Union &c.," *Phil. Mag.* Jan. 1892, p. 28.)

\* Communicated by the Author.



In a more recent investigation, "On Changes of Electromotive Force, Volume, and Temperature by Mixing Electrolytes" (see *Proc. Birm. Phil. Soc.* vol. viii. p. 28), I have further shown that if, instead of a single mixture of two solutions, a couple of such mixtures, isomeric with each other (for instance  $\text{HCl} + \text{NaBr}$ , and  $\text{HBr} + \text{NaCl}$ ), was employed, under certain conditions, in all the 25 cases of mixtures of Acids + Salts and of Salts + Salts which were examined, the two mixtures yielded the same amount of electromotive force, and therefore formed the same final product during the act of mixing; in each case the ingredients of the two mixtures started with different total amounts of energy, but arrived at the same final molecular and chemical constitution; each different isomeric couple, however, gave a different final amount. In other researches I found that if the solutions were extremely dilute and the "voltaic balance" method was employed, one of the two mixtures did not at once pass to the same final state, but gave a very different amount of voltaic energy from the other, especially if a free halogen formed part of the mixture. A list of unstable mixtures, as found by the voltaic balance method, has been given in a research on the "Relative Amounts of Available Voltaic Energy of Aqueous Solutions" (*Proc. Birm. Phil. Soc.* vol. vii. 1889, p. 47).

In the present research I have further examined the circumstances which influence the conditions of instability and of chemical and molecular equilibrium of such mixtures. The circumstances examined are:—1st, The influence of a halogen and a salt; 2nd, of a halogen and two salts; 3rd, of time upon the latter; 4th, of heating such a mixture; 5th, of doubling the amount of the halogen; 6th, of halving the amount of the two salts; 7th, of two different halogens and a salt; 8th, of a halogen and an acid; 9th, of two halogens and an acid; 10th, influence of one halogen and two acids; 11th, of halogens and an alkali with aluminium, tin, and zinc, as positive metals; and 12th, of heating the halogens with an alkali.

The method employed of measuring the electromotive force was that of opposition with a thermopile of iron and german silver and an astatic galvanometer, as in several of the previous researches (see more particularly "A Method of Measuring Loss of Energy due to Chemical Union, &c.," *Phil. Mag.* Jan. 1892, p. 28). The positive metal of the voltaic couple used in the experiments of Tables I. to X. and XIII. to XV. was of zinc, and in Table XI. of aluminium, and XII., of tin; the negative metal in all cases was platinum.

Distilled water was used in making all the solutions. In making them the following rules were observed:—In each Table, Nos. I. to X. and XIII. to XV., under the head of “Ingredients,” each ingredient—halogen, acid, or salt, as the case might be—was dissolved in the proportion of one equivalent weight in grains of the absolute substance in one unit quantity or 511,500 grains of water; in Tables XI. and XII. the proportion of water was 1800 grains. Under the head of “Mixtures,” an equivalent quantity in grains of *each* of the two or more substances forming the mixtures was *collectively* dissolved in a single unit quantity of water; but in Table V. two unit quantities in grains of one of the ingredients was included, as shown by the formulæ given. The substances employed were of a high degree of purity.

The experiments are divided into three chief sections, viz., Section A, Halogens + Salts; B, Halogens + Acids; and C, Halogens + Bases.

Section A.—HALOGENS + SALTS. Positive metal, Zinc.

TABLE I.—*Influence of a Halogen + a Salt.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br.	1·8706	Br + KOL	1·7276	1·5450	Gain ·1826 =	11·81
KOL	1·1927					
OL	1·9250	Cl + KBr.	„	1·3323	„ ·3953	29·67
KBr.	1·1556					
I.	1·4410	I + KOL	1·40156	1·3501	Gain ·05146 =	3·81
KI.	1·1470	Cl + KI.	„	1·2840	„ ·11756	9·15
		I + KBr.	1·3844	1·3029	Gain ·0815 =	6·25
		Br + KI.	„	1·3823	„ ·0021	·15

In each of these three cases of isomeric couples, each of the two mixtures gave the same amount of electromotive force, and had therefore acquired the same chemical and molecular composition at once on mixing.

TABLE II.—*Influence of a Halogen + two Salts.*

Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl + (KBr + KI).	1·5274	1·2376	Gain ·2898 =	23·41
Br + (KCl + KI).	1·4702	1·3101	„ ·1601	12·22
I + (KCl + KBr).	1·3787	1·2806	„ ·0981	7·65

The additional salt in each of these three cases of isomeric mixture prevented the mixture from at once attaining a fixed or final chemical and molecular constitution.

N.B. Compare the results with those of Tables III. and IV.

TABLE III.—*Influence of Time.*

	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
After standing 24 hours.	Cl+(KBr+KI).	1.37868	1.2376	Gain .14108 =	11.37
" " "	Br+(KCl+KI).	"	1.3101	" .0685	5.22
" " "	I+(KCl+KBr).	"	1.2806	" .0980	7.65

By standing a sufficient period of time at ordinary atmospheric temperature, the first two solutions of Table II. lost energy, and acquired the same chemical and molecular composition as the third one, *i. e.*, the one having the smallest electromotive force; these two mixtures therefore were in an unstable condition.

TABLE IV.—*Influence of Heating.*

	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
After heating.	Cl+(KBr+KI).	1.3701	1.2376	Gain .1325 =	10.70
" "	Br+(KCl+KI).	1.3844	1.3101	" .0743	5.67
" "	I+(KCl+KBr).	1.35294	1.2806	" .0723	5.65

Each mixture, newly made, was heated to 90° C. during 15 minutes in a stoppered glass flask and then cooled. In each case the percentage of gain of electromotive force which had occurred during the mixing was largely reduced, but least so with the last liquid. These results indicate that all three of these mixtures were more or less unstable, the first one the most and the last one the least so, that neither of them had completely attained the most fixed chemical and molecular condition, and that heating caused a rapid change in each to a fixed state. The chemical change and the final state arrived at evidently depend upon the temperature; even at 16° C. a slow change occurs, see Table III.

TABLE V.—*Influence of Doubling the Amount of the Halogen.*

Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
2Cl+(KBr+KI).	1.62178	1.3113	Gain .31048 =	23.67
2Br+(KCl+KI).	"	1.5684	" .05338	3.40

Doubling the amount of the halogen caused each of the two mixtures to assume the same chemical and molecular composition immediately on mixing. It appears from a comparison of these results and those of Table I. with those of Table II., that the condition of chemical and molecular equilibrium depends upon the proportion of free halogen to that of the salts. If the proportion of the halogen to the total of the salt was 1 eqt. to 1 eqt. as in Table I., or 2 eqts. to 2 eqts. as in Table V., each mixture at once suffered a change and attained a fixed state; but if it was 1 eqt. of halogen to 2 eqts. of the salt, as in Table II., each mixture was in a condition of instability, and was prevented from assuming at once the fixed state, but it was not prevented from undergoing a gradual change at atmospheric temperature (see Table III.); the additional proportion of salt therefore only *hindered* the change.

The degree of solubility of iodine in water was too small to enable a double proportion of it to be used.

TABLE VI.—*Influence of Halving the Amount of the Salts.*

Mixture.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
I+.5(KCl+KBr).	1.41014	1.3203	Gain .0898	= 6.8

The proportion of gain of mean amount of electromotive force is somewhat less than in the comparison case in Table II., as if diminishing the proportion of salt to halogen increased the amount of chemical and molecular change and assisted the mixture to attain a fixed state, similar to the effect of doubling the amount of the halogen, as shown in Table V.

TABLE VII.—*Influence of Two Halogens + a Salt.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl+Br.	1.8992	(Cl+Br)+KI.	1.63036	1.4556	Gain .17476	= 12.00
Cl+I.	1.7133	(Cl+I)+KBr.	1.62178	1.4775	" .14428	9.76
Br+I.	1.69338	(Br+I)+KCl.	"	1.5615	" .06028	3.80

The amounts of electromotive force obtained by means of experiment in the three instances are so nearly alike that they may be regarded as identical. On comparing the results

with those of Table I., we find that whether the mixtures contained a single halogen or two different ones, each of the mixtures which were isomeric to each other at once attained the same final state; and on comparing them with those of Tables I. and II., it appears that whilst an additional salt hindered the chemical and molecular change, the addition of a second halogen did not impede the change, probably because the halogen was free and had greater chemical energy.

In a previous research (Phil. Mag. Jan. 1892, p. 49) I have examined the influence upon the electromotive force of a cadmium platinum couple of heating aqueous solutions of chlorine, bromine, and iodine alone, during successive periods of time, until a state of equilibrium was attained, and have shown the amounts of change thereby produced; the strength of solution then employed was one equivalent weight of the halogen in grains in 449,500 grains of water. These experiments with the three halogens showed the limits of the amount of chemical and molecular change produced in their aqueous solutions by means of heat.

Section B.—HALOGENS + ACIDS. Positive metal, Zinc.

TABLE VIII.—*Influence of a Halogen + an Acid.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl.	1·9250					
HBr.	1·30718	Cl + HBr.	1·73332	1·4954	Gain ·2379	= 15·9
Br.	1·8706					
HCl.	1·35866	Br + HCl.	1·73904	1·7102	„ ·0288	1·68
HI.	1·18134	Cl + HI.	1·41014	1·3428	Gain ·06734	= 5·01
I.	1·4410	I + HCl.	„	1·4226	Loss ·0125	·87
		Br + HI.	1·40156	1·4464	Loss ·0448	= 3·09
		I + HBr.	„	1·3888	Gain ·01276	·91

With the two mixtures of the first isomeric couple the electromotive forces were unsteady, and the amounts obtained by means of experiment are so nearly alike that they may be regarded as identical. In all three cases the two isomeric mixtures of each couple appear to have at once attained the same final chemical and molecular composition and state of equilibrium.

TABLE IX.—*Influence of Two Halogens and One Acid.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Cl+Br.	1·8992	HI+(Cl+Br).	1·6847	1·5249	Gain ·1598 =	10·48
Cl+I.	1·7133	HBr+(Cl+I).	1·7076	1·5814	" ·1262	7·98
Br+I.	1·69338	HCl+(Br+I).	1·6847	1·6464	" ·0383	2·33

The additional halogen did not prevent the three mixtures attaining nearly the same final state.

TABLE X.—*Influence of One Halogen and Two Acids.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
HBr+HI.	1·27858	Cl+(HBr+HI).	1·5274	1·3751	Gain ·1523 =	11·11
HCl+HI.	1·3329	Br+(HCl+HI).	1·4702	1·5119	Loss ·0417	2·76
HCl+HBr.	1·3529	I+(HCl+HBr).	1·4072	1·4015	Gain ·0067	·40

The additional acid retarded the attainment of a state of stable chemical equilibrium similar to the effect of an additional salt (see Table II.).

### Section C.—HALOGENS + BASES.

Strength of solution = 1 equivalent weight in grains in 1800 grains of water.

TABLE XI.—*With Al as Positive Metal.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water.	1·5816					
KHO solution.	1·3814	Br+KHO.	1·5244	1·4991	Gain ·0253 =	1·68
After heating 1 min. to 90° C. ....		" "	1·5101	"	" ·0110	73

TABLE XII.—*With Sn as Positive Metal.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water.	1·2213					
KHO solution.	·9210	Br+KHO.	·9496	1·0976	Loss ·1480 =	13·49
After heating 1 min. to 90° C. ....		" "	·9067	"	" ·1909	17·40

The bromine solution used in Tables XI. and XII. was not rendered colourless by the alkali; the resulting mixture gave with test-paper an alkaline reaction followed by a bleaching effect; its colour was not visibly altered by heating, nor by the addition of a second equivalent of the alkali. Both by means of an aluminium positive metal and a tin one a loss of electromotive force caused by heating the mixture was detected, and it was shown that the most stable condition of chemical equilibrium was not attained during the act of mixing.

*With Zn as Positive Metal.*

Strength of Solution = 1 equivalent weight in grains in 511,500 grains of water.

TABLE XIII.—*Chlorine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
H <sub>2</sub> O.	1.1270					
KHO solution.	1.0755					
Cl water.	1.9250	Cl + KHO.	1.8420	1.4055	Gain .4365 =	31.06
min.						
After heating 1 to 98° C.		" "	1.6990	"	" .2935	20.88
" " 1 " "		" "	1.5274	"	" .1219	8.67
" " 5 " "		" "	1.3129	"	Loss .0926	6.59
" " 30 " "		" "	1.17216	"	" .2334	16.61
" " 30 " "		" "	1.13270	"	" .2728	19.40

The solution of Cl + KHO in these experiments required much more prolonged heating than one of Cl alone, in order to reduce the electromotive force to the smallest amount and to complete the chemical and molecular change. Whilst also with the mixture of Cl + KHO the electromotive force was finally reduced nearly to that given by water alone; with a solution of Cl alone it finally remained constant at a number nearly double that given by water (*ibid.*).

TABLE XIV.—*Bromine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Br water	1.8706	Br + KHO.	1.69614	1.4696	Gain .22654 =	15.41
min.						
After heating 1 to 98° C.		" "	1.61320	"	" .1436	9.77
" " 1 " "		" "	1.51882	"	" .04922	3.35
" " 5 " "		" "	1.19420	"	Loss .2754	18.70
" " 30 " "		" "	1.1270	"	" .3426	23.31

The electromotive force was finally reduced to that of water, and the chemical and molecular change appeared to be nearly complete.

TABLE XV.—*Iodine water + KHO.*

Ingredients.	E.M.F.	Mixtures.	E.M.F.	Calculated E.M.F.	Change of E.M.F.	Per cent.
Iodine water	1.4416	I+KHO.	1.3844	1.3295	Gain .0540 =	4.136
min.						
After heating 1 to 98° C.		" "	1.3272	"	Loss .0023	.1730
" " 1 " "		" "	1.2843	"	" .0452	3.400
" " 5 " "		" "	1.1942	"	" .1353	10.17
" " 30 " "		" "	1.1270	"	" .2025	15.23

Similar remarks may be made respecting the results of this Table as about those of Table XIV.

In each of these three tables the process of heating caused a gradual loss, and at a diminishing rate of electromotive force; and each of the liquids appeared to finally acquire a fixed chemical and molecular state. The total percentage losses of mean amount of electromotive force with the three mixtures were as follows:—with Cl+KHO, 50.4; with Br+KHO, 38.7; and with I+KHO, 19.30.

#### *General Remarks and Conclusions.*

1. The mixtures employed in this research may be divided into two classes, viz., those which spontaneously change with such rapidity that they at once attain on mixing a comparatively fixed state of chemical and molecular equilibrium, and those which only slowly change and attain such a state.

2. The results of the present research and of previous ones show, that with mixtures of acids+salts, and of salts+salts, a fixed state of equilibrium was in nearly all cases immediately attained; but with halogens+salts, halogens+acids, and halogens+bases, a greater or less degree of retardation of attainment of such a state frequently happened.

3. According to the results given in Tables V. and VI. compared with those of Table I., doubling the degree of concentration of the solution did not produce any conspicuous effect upon the state of chemical equilibrium.

4. The results of Table III. indicate that with the particular mixtures there employed, a gradual change by lapse of time occurred, and each liquid attained a state of comparative equilibrium in 24 hours.

5. The great influence of temperature is shown in a number of cases in Tables IV., XI., XII., XIII., XIV., and XV.; in all cases it acted so as to promote chemical and molecular



change, and enabled the mixtures to arrive at a fixed state. The results of previous experiments (Phil. Mag. Jan. 1892, p. 49) show that the action of the higher temperature was upon the halogen present. In all cases of heating aqueous solutions, either of Cl, Br, or iodine alone (*ibid.*), or of Cl + (KBr + KI), Br + (KCl + KI), or I + (KCl + KBr), Table IV. ; Br + KHO, with a positive metal of aluminium or of tin, Tables XI. and XII. ; Cl + KHO, Br + KHO, or I + KHO, with zinc as a positive metal—a relative *loss* of electromotive force took place, and a more fixed state of chemical equilibrium was attained.

6. The results of Table I. show that if the ingredients of a mixture of a halogen and a salt in water were in the proportion of their chemical equivalents, the complete change and attainment of a fixed condition of equilibrium was promoted. If, however, as in Table II., the saline ingredient was in excess, the change to a fixed state of chemical equilibrium was retarded. But if, as in Tables V. and VI., the electro-negative one was in excess, the changes were not retarded.

7. Mixtures of halogens and acids in chemically equivalent proportions, as in Table VIII., acted much like those of halogens and salts in Table I., *i. e.*, their solutions at once attained a fixed or final state of chemical equilibrium on mixing ; but an additional acid, like an additional salt, retarded the chemical change (see Table X.).

8. Comparison of the results given in Tables I. and II. with those in Tables VII. and IX., shows that whilst doubling the proportion of salt to halogen retarded the change, doubling that of the halogen had no such effect.

9. Comparison also of the results given in Tables XIII., XIV., and XV. with those obtained with solutions of the halogens alone (Phil. Mag. Jan. 1892, p. 49) shows that the addition of a caustic alkali to a solution of a halogen considerably retarded the rate of change which occurred on heating. An inspection of the results in Tables XIII., XIV., and XV., further shows that the greatest retardation occurred with chlorine and the least with iodine ; probably because the chlorine had the largest amount of molecular motion to be retarded.

10. The leading idea in all these cases is *the degree of freedom of molecular motion*, and the most general conclusion is, that the smaller the degree of freedom of such motion of the halogen molecules, the greater the retardation of chemical change ; heat therefore increases, and the presence of dissolved alkalis, salts, or acids decreases the rate of change and retards the attainment of a fixed state of chemical equilibrium.

XXXVII. *Note on the Resistance and Self-Induction of Branched Circuits.* By Prof. A. ANDERSON, M.A.\*

ON page 134 of Fleming's 'Alternate Current Transformer,' vol. i., the values are given of the effective resistance and inductance of a system of conductors connected in parallel, and acted on by an impressed electromotive force varying according to a simple harmonic law. The conductors are supposed to have no mutual induction. The results are taken from a paper by Lord Rayleigh in the Philosophical Magazine of May 1886, to which the reader is referred.

The following method of obtaining these results, although it really does not differ much from that given in Lord Rayleigh's paper, will perhaps be more easily understood.

Let the resistances of the conductors be  $R_1, R_2, R_3, \dots R_n$ , the coefficients of self-induction  $L_1, L_2, L_3, \dots L_n$ , and suppose the impressed electromotive force to be  $E \sin pt$ . The currents in the branches may be denoted by  $I_1 \sin(pt - \theta_1), I_2 \sin(pt - \theta_2), \dots I_n \sin(pt - \theta_n)$ . Hence, if  $i$  denote the total current, we have

$$i = \sin pt \sum I \cos \theta - \cos pt \sum I \sin \theta.$$

Now, since

$$\begin{aligned} E \sin pt &= R_1 I_1 \sin(pt - \theta_1) + p L_1 I_1 \cos(pt - \theta_1) \\ &= R_2 I_2 \sin(pt - \theta_2) + p L_2 I_2 \cos(pt - \theta_2) \\ &= \dots, \end{aligned}$$

we have

$$\begin{aligned} E &= R_1 I_1 \cos \theta_1 + p L_1 I_1 \sin \theta_1, \\ 0 &= p L_1 I_1 \cos \theta_1 - R_1 I_1 \sin \theta_1, \end{aligned}$$

whence

$$I_1 \cos \theta_1 = \frac{E R_1}{R_1^2 + p^2 L_1^2}, \quad I_1 \sin \theta_1 = \frac{p E L_1}{R_1^2 + p^2 L_1^2};$$

and similar expressions hold for  $I_2 \cos \theta_2, I_2 \sin \theta_2$ , &c.

Hence

$$i = E \sin pt \sum \frac{R}{R^2 + p^2 L^2} - p E \cos pt \sum \frac{L}{R^2 + p^2 L^2},$$

or

$$i = A E \sin pt - p B E \cos pt, \text{ where } A \text{ is written for}$$

$$\sum \frac{R}{R^2 + p^2 L^2}, \text{ and } B \text{ for } \sum \frac{L}{R^2 + p^2 L^2}.$$

\* Communicated by the Author.

Now, denoting the effective resistance of the system by  $R'$  and the inductance by  $L'$ , we have

$$E \sin pt = R'i + L' \frac{di}{dt},$$

or

$$\sin pt = (AR' + p^2 BL') \sin pt + p(L'A - R'B) \cos pt;$$

and, therefore,

$$L'A - R'B = 0,$$

$$AR' + p^2 BL' = 1,$$

so that

$$R' = \frac{A}{A^2 + p^2 B^2}, \quad L' = \frac{B}{A^2 + p^2 B^2},$$

which are the results quoted.

We may employ the same method to find the effective resistance and inductance in the case where the conductors have mutual induction. Let  $M_{rs}$ , or  $M_{sr}$ , denote the coefficient of mutual induction between the conductors  $r$  and  $s$ . It will now be convenient to discontinue the use of the symbol  $L$ , and to denote the coefficient of self-induction of the conductor  $r$  by  $M_{rr}$ . We have, in this case,

$$\begin{aligned} E \sin pt &= R_1 I_1 \sin (pt - \theta_1) + p[M_{11} I_1 \cos (pt - \theta_1) \\ &\quad + M_{12} I_2 \cos (pt - \theta_2) + \dots + M_{1n} I_n \cos (pt - \theta_n)] \\ &= R_2 I_2 \sin (pt - \theta_1) + p[M_{21} I_1 \cos (pt - \theta_1) \\ &\quad + M_{22} I_2 \cos (pt - \theta_2) + \dots + M_{2n} I_n \cos (pt - \theta_n)] \\ &= \dots \end{aligned}$$

Hence

$$\begin{aligned} E &= R_1 I_1 \cos \theta_1 + p[M_{11} I_1 \sin \theta_1 + M_{12} I_2 \sin \theta_2 + \dots + M_{1n} I_n \sin \theta_n], \\ 0 &= R_1 I_1 \sin \theta_1 - p[M_{11} I_1 \cos \theta_1 + M_{12} I_2 \cos \theta_2 + \dots + M_{1n} I_n \cos \theta_n]. \end{aligned}$$

Denoting

$$I_1 \cos \theta_1, I_2 \cos \theta_2, \dots \text{ by } x_1, x_2, \dots,$$

and

$$I_1 \sin \theta_1, I_2 \sin \theta_2, \dots \text{ by } y_1, y_2, \dots,$$

we have the equations

$$E = R_1 x_1 + p \sum_{r=1}^{r=n} M_{1r} y_r = R_2 x_2 + p \sum_{r=1}^{r=n} M_{2r} y_r = \dots = \dots,$$

$$0 = R_1 y_1 - p \sum_{r=1}^{r=n} M_{1r} x_r = R_2 y_2 - p \sum_{r=1}^{r=n} M_{2r} x_r = \dots = \dots$$

Substituting in the former equations the values of  $y_1, y_2, \dots$  found from the latter, we get the system

$$\begin{aligned} E &= R_1 x_1 + p^2 \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} \frac{M_{1r} M_{rs}}{R_r} x_s \\ &= R_2 x_2 + p^2 \sum_{r=1}^{r=n} \sum_{s=1}^{s=n} \frac{M_{2r} M_{rs}}{R_r} x_s \\ &= \dots \end{aligned}$$

If we denote

$$\sum_{r=1}^{r=n} \frac{M_{\mu r} M_{rs}}{R_r} \text{ by } P_{\mu s},$$

we get

$$\begin{aligned} \frac{E}{p^2} &= \frac{R_1 x_1}{p^2} + \sum_{r=1}^{r=n} P_{1r} x_r \\ &= \frac{R_2 x_2}{p^2} + \sum_{r=1}^{r=n} P_{2r} x_r \\ &= \dots \end{aligned}$$

Hence

$$x_1 = \frac{EQ_1}{p^2 \Delta}, \quad x_2 = \frac{EQ_2}{p^2 \Delta}, \quad \dots \quad x_r = \frac{EQ_r}{p^2 \Delta},$$

where

$$\Delta = \begin{vmatrix} P_{11} + \frac{R_1}{p^2}, & P_{12}, & P_{13}, & \dots & P_{1n} \\ P_{21}, & P_{22} + \frac{R_2}{p^2}, & P_{23}, & \dots & P_{2n} \\ P_{31}, & P_{32}, & P_{33} + \frac{R_3}{p^2}, & \dots & P_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ P_{n1}, & P_{n2}, & P_{n3}, & \dots & P_{nn} + \frac{R_n}{p^2} \end{vmatrix},$$

and  $Q_r$  is the result of equating to unity the terms in the  $r$ th row or  $r$ th column of this determinant.

It follows, then, immediately, that

$$y_1 = \frac{EU_1}{p\Delta}, \quad y_2 = \frac{EU_2}{p\Delta}, \quad \dots \quad y = \frac{EU_r}{p\Delta}, \quad \dots,$$

where

$$U_r = \frac{1}{R_r} \sum_{s=1}^{r=n} M_{rs} Q_s.$$

Now, as before, we have

$$i = \sin pt \Sigma x - \cos pt \Sigma y,$$

and, therefore,

$$E \sin pt = R'(\sin pt \Sigma x - \cos pt \Sigma y) + pL'(\cos pt \Sigma x + \sin pt \Sigma y),$$

whence

$$E = R' \Sigma x + pL' \Sigma y,$$

$$0 = pL' \Sigma x - R' \Sigma y,$$

and

$$R' = \frac{E \Sigma x}{(\Sigma x)^2 + (\Sigma y)^2}, \quad L' = \frac{E \Sigma y}{(\Sigma x)^2 + (\Sigma y)^2},$$

or

$$R' = \frac{p^2 \Delta \Sigma Q}{(\Sigma Q)^2 + p^2 (\Sigma U)^2}, \quad L' = \frac{p^2 \Delta \Sigma U}{(\Sigma Q)^2 + p^2 (\Sigma U)^2}.$$

In the simple case of two branches of resistances  $R$  and  $S$ , coefficients of self-induction  $L$  and  $N$ , and coefficient of mutual induction  $M$ , we easily find

$$\Delta = \frac{R^2 S^2 + p^2 (2M^2 RS + L^2 S^2 + N^2 R^2) + p^4 (LN - M^2)^2}{p^4 RS},$$

$$\Sigma Q = \frac{RS(R+S) + p^2 S(L-M)^2 + p^2 R(N-M)^2}{p^2 RS},$$

and

$$\Sigma U = \frac{2MRS + LS^2 + NR^2 + p^2 (LN - M^2)(L+N-2M)}{p^2 RS},$$

The values of  $L'$  and  $R'$  are obtained by substitution. If  $p=0$ , we see by inspection that

$$R' = \frac{RS}{R+S} \quad \text{and} \quad L' = \frac{2MRS + LS^2 + NR^2}{(R+S)^2},$$

and if  $p=\infty$ , that

$$R' = \frac{S(L-M)^2 + R(N-M)^2}{(L+N-2M)^2}, \quad L' = \frac{LN-M^2}{L+N-2M}.$$

XXXVIII. *Remarks on Maxwell's Investigation respecting Boltzmann's Theorem.* By Lord RAYLEIGH, Sec. R.S.\*

THE investigation in question, which was published by Maxwell in the 12th volume of the Cambridge Philosophical Transactions† only a short time before his death, has been the subject of some adverse criticism at the hands of Sir W. Thomson‡ and of Mr. Bryan§. The question is indeed a very difficult one; and I do not pretend to feel complete confidence in the correctness of the view now to be put forward. Nevertheless, it seems desirable that at the present stage of the discussion some reply to the above-mentioned criticisms should be hazarded, if only in order to keep the question open.

The argument to which most exception has been taken is that by which Maxwell (Reprint, p. 722) seeks to prove that the mean kinetic energy corresponding to every variable is the same. In the course of it, the expression  $T$  for the kinetic energy is supposed to be reduced to a sum of squares of the component momenta, an assumption which Mr. Bryan characterizes as fallacious. But here it seems to be overlooked that Maxwell is limiting his attention to systems in a *given configuration*, and that no dynamics is founded upon the reduced expression for  $T$ . The reduction can be effected in an infinite number of ways. We may imagine the configuration in question rendered one of stable equilibrium by the introduction of suitable forces proportional to displacements. The principal modes of isochronous vibration thus resulting will serve the required purpose. I do not see the applicability to this argument of the warning quoted from Routh's 'Rigid Dynamics.' Perhaps the objection is felt that the conclusion cannot be true in the absence of a complete specification of the variables. This is a point that may require further examination. I admit that the argument seems to imply that the conclusion possesses something of an invariant character.

The nature of the question may be illustrated by an example approximately realized in the billiard-table, viz. the path of an elastic particle moving in a plane without loss of energy and

\* Communicated by the Author.

† 'Reprint,' vol. ii. p. 713.

‡ Proc. Roy. Soc. June 1891.

§ "On the Present State of our Knowledge of Thermodynamics," Brit. Assoc. Report, 1891. I am indebted to the author for an advance copy of this valuable report.

limited within an enclosure. The fundamental assumption is that, apart from exceptional cases, the particle, starting from a given point, will sooner or later traverse that point in *every direction*; and the conclusion founded upon this assumption is that in the long run all directions through the point are equally favoured. I do not see that there is here anything to be specially surprised at. If the premises are admitted, the conclusion seems natural enough.

In another part of his investigation Maxwell puts forward under the same reserves the more general hypothesis that not merely does the system pass through a given configuration with every possible system of velocities consistent with the energy condition, but also through every configuration which can be reached without violation of the same condition. In the billiard-table example this means that every part of the table is reached sooner or later, and, as we have seen, every part that is reached is traversed as much in one direction as in another. In this case, where there is no potential energy, we may indeed go further. Maxwell's equation (41) shows that any part of the table is occupied in the long run as much as any other; so that all points, as well as all directions, are equally probable.

To my mind the difficulty of Maxwell's investigation lies more in the premises than in the deductions\*. It is easy to propose particular cases for which the hypothesis is manifestly untrue. For example, if the table be circular, a particle projected otherwise than along a diameter will leave a central circular area uninvaded, and in the outer zone will not pass through a given point in every direction, even when the projection is such that the path is not re-entrant. The question is how far the considerations advanced by Maxwell justify us in putting aside these cases as too exceptional to interfere with the general proposition, which, at any rate in its application to physics, is essentially one of probability.

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Having found Maxwell's demonstration of the fundamental theorem

$$dq_1' \dots dq_n' dp_1' \dots dp_n' = dq_1 \dots dq_n dp_1 \dots dp_n$$

difficult to follow, I have sought to simplify it by an arrangement such that the initial and final times  $t'$  and  $t$  may be

\* The particular case for which Burnside obtained a result inconsistent with Maxwell's conclusions is emphasized by Mr. Bryan. But Mr. Burbury is of opinion that the discordant result depends upon an error of calculation, and that when this is set right the discrepancy disappears (Proc. Roy. Soc., November 19, 1891, p. 196).

358 *On Maxwell's Investigation of Boltzmann's Theorem.*

considered as absolutely fixed throughout the discussion. The following, dependent upon the substitution for the "action"  $A$  of Hamilton's "principal function"  $S$ , seems to meet the requirements of the case. By definition,

$$S = \int_r^t (T - V) dt = \frac{1}{2}A - \int_r^t V dt;$$

and, as in Thomson and Tait's 'Natural Philosophy,' § 319,

$$\begin{aligned} \delta S &= \frac{1}{2}\delta A - \int_r^t \delta V dt \\ &= \frac{1}{2}\{\Sigma m(\dot{x}\delta x + \dots)\} - \frac{1}{2}[\Sigma m(\dot{x}\delta x + \dots)] \\ &\quad + \frac{1}{2}\int_r^t dt[\delta T + \delta V - 2\delta V]; \end{aligned}$$

so that

$$\delta S = \{\Sigma m(\dot{x}\delta x + \dots)\} - [\Sigma m(\dot{x}\delta x + \dots)],$$

or in generalized coordinates

$$\delta S = \Sigma p \delta q - \Sigma p' \delta q'. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this equation all the motions contemplated are unconstrained, and occupy the fixed time  $t-t'$ . The total energy  $E$  is variable from one motion to another, and  $S$  is to be regarded as a function of the  $q$ 's and  $q$ 's.

The initial and final momenta are thus expressed by means of  $S$  in the form

$$p_r' = -\frac{dS}{dq_r'}, \quad p_r = \frac{dS}{dq_r}; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that

$$\frac{dp_r'}{dq_s} = -\frac{d^2S}{dq_r' dq_s} = -\frac{dp_s}{dq_r'}. \quad . \quad . \quad . \quad . \quad (3)*$$

Thus, using  $S$  with  $t-t'$  constant, instead of (as in Maxwell's investigation)  $A$  with  $E$  constant, we get

\* As an example the motion of a particle in two dimensions about a centre of force may be considered.  $q_r, q_s$  are then the rectangular co-ordinates of the particle at a fixed time  $t$ ;  $q_r', q_s'$  the coordinates at the fixed time  $t'$ , while  $p_r, p_s$  and  $p_r', p_s'$  are the component velocities at the same moments.

In equation (3)  $r$  and  $s$  may be identical.



$$dq_1' \dots dq_n' dp_1' \dots dp_n' = dq_1' \dots dq_n' dq_1 \dots dq_n$$

$$\times \begin{vmatrix} \frac{dp_1'}{dq_1} & \dots & \frac{dp_n'}{dq_1} \\ \vdots & \ddots & \vdots \\ \frac{dp_1'}{dq_n} & \dots & \frac{dp_n'}{dq_n} \end{vmatrix} \dots \dots \dots (4)$$

On the left side the motion is defined by the initial  $q$ 's and  $p$ 's at time  $t'$ ; on the right by the initial and final  $q$ 's and by  $t-t'$  (not  $E$ , which is a dependent variable).

In like manner

$$dq_1 \dots dq_n dp_1 \dots dp_n = dq_1' \dots dq_n' dq_1 \dots dq_n$$

$$\times \begin{vmatrix} \frac{dp_1}{dq_1'} & \dots & \frac{dp_n}{dq_1'} \\ \vdots & \ddots & \vdots \\ \frac{dp_1}{dq_n'} & \dots & \frac{dp_n}{dq_n'} \end{vmatrix} \dots \dots \dots (5)$$

By the relation (3) proved above the two determinants in (4) and (5) are equal, and thus

$$dq_1' \dots dq_n' dp_1' \dots dp_n' = dq_1 \dots dq_n dp_1 \dots dp_n, \quad (5)$$

the required conclusion.

February 20.

**XXXIX.** *On an Experiment Illustrative of the Formation of Rocking Stones.* By CHARLES TOMLINSON, F.R.S.\*

**I**N an article on the "Weathering of Rocks" (Phil. Mag. Dec. 1888), I noticed the explanation given by Dr. Paris and Mr. Justice Grove on the formation of logging or rocking stones, and stated that the process described by them might be imitated by small blocks of camphor freely exposed to evaporation in the air.

Camphor is now sold in neatly cut parallelopipeds, oblong and square. A square block,  $1\frac{1}{4}$  inch to the side, and half an inch thick was superposed upon one of similar dimensions (fig. 1), and placed in the glass pan of a pair of scales close to

\* Communicated by the Author.

the window of an inhabited room. The initial weight of the pile at the beginning of the experiment at 5 P.M. on the 17th October last was 422 grains; on the 18th, at 11.30 A.M., the weight was 416 grains.

	grains.		grains.
Oct. 19th, at 11, . .	406	Nov. 1st, at 10.45, . .	259
20th, „ 10.30, . .	391	2nd, „ 10.30, . .	253
21st, „ 11, . .	380	3rd, „ 10, . .	243
22nd, „ 12.30, . .	366	4th, „ 11.30, . .	235
23rd, „ 1.30, . .	352	5th, „ 10.30, . .	226
24th, „ 10.30, . .	340	6th, „ 10.30, . .	219
25th, „ 10.15, . .	330	7th, „ 11.30, . .	210
26th, no observation.		8th, „ 10.30, . .	202
27th, at 10.30, . .	307	9th, „ 10.45, . .	195
28th, „ 12, . .	296	10th, no observation.	
29th, „ 11.30, . .	286	11th, at 11, . .	183
30th, „ 10, . .	276	12th, „ 10.30 . .	178
31st, „ 10.30. . .	269		

During these observations the changes remarked by Mr. Justice Grove as applicable to two slabs of stone applied equally well to the two slabs of camphor. "If we suppose a slab of stone [camphor] lying on another, both having flat surfaces, the disintegration produced by changes of weather, of temperature, &c., [evaporation] would act to the greatest extent at the corners, and next to them at the edges, because those parts expose respectively the greater surfaces compared with the bulk of the stones [camphor]. This would tend to

Fig. 1.

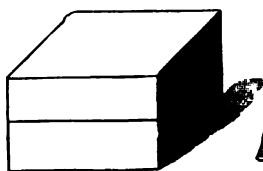


Fig. 2.



Fig. 3.



round off all the angles, and gradually change the rhomb more or less towards an oblate spheroid."

The above description applies with great accuracy to the changes that took place in the superposed blocks of camphor (fig. 2), whether of the dimensions above indicated or on larger blocks, namely  $2\frac{1}{2}$  inches. In such case the form became reduced in the course of many months to flattened oblate spheroids. In the case of the smaller masses which were weighed from day to day, after the solid angles and

edges had been removed, evaporation took place chiefly from the top piece, which being more freely exposed diminished far more rapidly than the lower piece, which it partially sheltered and protected from evaporation. Hence there was a gradual decline in the loss suffered from day to day, namely, from 10 or 12 grains to 3 or 4. This decline was apparently due to the diminution of surface exposed, rather than to the state of the weather outside. The temperature was noted when the weight was taken, both with the wet and dry bulb ; but being in an inhabited room it did not greatly vary, and the external atmospheric conditions seemed to have but little influence. The experiment was terminated on the 9th December, when the two fragments of camphor were weighed separately. The lower piece weighed 54 grains and the upper 14. It will be seen from fig. 3 that the upper fragment rests upon a kind of point due to the loss of matter from the upper side of the lower piece, and the under side of the upper piece around the point of contact, and this is exactly what takes place in the logging or logan stones by the slower action of weathering. It will be seen that the conditions are now fulfilled to allow the upper piece to be rocked upon the lower.

An interesting result was obtained by inserting a square piece of filtering paper between another pair of the  $1\frac{1}{4}$  inch camphor blocks. The two blocks were held between the finger and thumb, and the paper between them was trimmed along the four sides with a small pair of scissors, so that the paper projected over the lower block only to the extent of half the thickness of the scissor blades. The blocks, put on a glass plate, were placed on a high shelf in an inhabited room, and were left undisturbed for many weeks, when it was found that the slight paper projection had been sufficient to protect the lower block from evaporation, so as to preserve the solid angles and edges.

It was formerly supposed that light had a subtle but powerful influence in promoting crystallization and producing deposits of camphor and other volatile bodies on the most illuminated side of the closed vessels containing them. This idea was favoured in our text-books by such recent authorities as Daniell, Brande, and Miller. In the *Philosophical Magazine* for November 1862, I showed by a number of experiments that these deposits are made, not on the most illuminated side of the vessel, but on the coldest side. With respect to crystallization it was supposed that a saline solution would not deposit its salt if the vessel containing it were screened from the light. Thus Chaptal observed that by covering over

certain parts of the evaporating dish with black taffeta, so as entirely to exclude the light, crystals would creep up only on the side to which light had access. But the function of the screen was mistaken ; its action being to prevent evaporation, as may be seen in an experiment so contrived as to admit light freely, but exclude or limit the evaporating force. Fig. 4 represents two vessels, on different levels, each containing a

Fig. 4.



saline solution : they were placed on the ledge of a window facing the west, so as to be in the full light of day, and often in sunshine. The top vessel was half covered with a thin glass plate, which projected above and over one half of the lower vessel. The exposed half of each vessel had a crystalline deposit running round it. The left-hand glass contained a solution of acetate of lime. This is well adapted to the purpose of this test experiment. The glass being replenished every few days, large rounded cauliflower masses of great beauty are formed on the uncovered half of the glass, gradually swelling over and adhering to the outside. They are first white, but by exposure to the sun become of a delicate yellow, touched with a deep brown on the most projecting portions, while the solid in the dish is striated after the manner of certain fibrous minerals. The glasses may, however, contain a solution of almost any salt, and a deposit will be found on the uncovered half of either glass, and none on the covered half.

Highgate, 14th December, 1891.

XL. *Experiments upon Surface-Films.*By LORD RAYLEIGH, *Sec. R.S.\**

THE experiments here described are rather miscellaneous in character, but seem of sufficient interest to be worthy of record. The greater number of them have been exhibited in the course of lectures at the Royal Institution.

*The Behaviour of Clean Mercury.*

According to Marangoni's rule, water, which has the lower surface-tension, should spread upon the surface of mercury ; whereas the universal experience of the laboratory is that drops of water standing upon mercury retain their compact form without the least tendency to spread. To Quincke belongs the credit of dissipating the apparent exception. He found that mercury specially prepared behaves quite differently from ordinary mercury, and that a drop of water deposited thereon spreads over the whole surface. The ordinary behaviour is evidently the result of a film of grease, which adheres with great obstinacy.

The process described by Quincke is somewhat elaborate ; but my experience with water suggested that success might not be so difficult, if only the mistake were avoided of pouring the liquid to be tried from an ordinary bottle. In the early experiments upon the camphor movements difficulty seems to have been experienced in securing sufficiently clean water surfaces. The explanation is probably to be found in the desire to use distilled water, and to the fact that the liquid would usually be simply poured from a stock bottle into the experimental vessel. No worse procedure could be devised ; for the free surface in the bottle is almost sure to be dirty, and is transferred in great part to the vessel. In my experience water from the dirtiest cistern will exhibit the camphor movements, provided that it be drawn in the usual manner from a tap, and that the precaution be taken to give the vessel a preliminary rinsing.

In order to carry out the idea of drawing the liquid from underneath, an arrangement was provided like an ordinary wash-bottle, and was filled with tolerably clean mercury. As experimental vessels watch-glasses are convenient. They may be dipped into strong sulphuric acid, rinsed in distilled water, and dried over a Bunsen flame. When the glasses are cool they may be charged with mercury, of which the first

\* Communicated by the Author.

portion is rejected. Operating in this way there was no difficulty in obtaining surfaces upon which a drop of water would spread, although, from causes that could not always be traced, a certain proportion of failures was met with.

Exposure of the glasses to the atmosphere soon tells upon the success of the experiment, although on one occasion spreading occurred after a glass had stood (with protection from dust) for 20 hours. Even so short an exposure as 10 minutes was found to prejudice the condition of the mercury<sup>s</sup> surface. Although something here may have depended upon the special character of the sample of mercury, it will be advisable in repeating the experiment to pour the mercury at the last moment.

As might be expected, the grease which produces these effects is largely volatile. In many cases a very moderate preliminary warming of the watch-glass makes all the difference in the behaviour of the drop.

So far as I have observed, the spreading of the drop takes place always in a leisurely fashion. If a little powder of recently ignited magnesia be dusted over the mercury, there is no violent repulsion of the dust before the advancing water. But if a small drop of oil be substituted for the water, the powder is flashed away so quickly that the eye cannot follow the operation. The difference between the two cases appears to depend upon the atmospheric moisture. As soon as the mercury is poured, it coats itself with an aqueous film, and the subsequent spreading of the drop takes place upon a surface whose affinity for water is already largely satisfied. A drop of water that has spread and then partially gathered up again (as usually happens after a short interval) shows an interesting behaviour when breathed upon. The disk contracts somewhat, and then as the breath, which need hardly be visible, passes off, expands again; and thus a number of times. The temporary character of the effect indicates that it is due rather to the moisture of the breath than to any greasy contamination; a view confirmed by subsequent experiments, in which the breath was replaced by a current of pure air which had passed through warm water.

In the experiment with a powdered surface, the dust may be driven from the neighbourhood of a drop of petroleum by the action of vapour without actual contact of the liquids.

#### *Drops of Bisulphide of Carbon upon Water.*

The behaviour of a drop of  $\text{CS}_2$  placed upon clean water is also at first sight an exception to Marangoni's rule. So far

from spreading over the surface, as according to its lower tension it ought to do, it remains suspended in the form of a lens. And dust which may be lying upon the surface is not driven away to the edge upon the deposit of the drop, as would happen in the case of oil. A simple modification of the experiment suffices, however, to clear up the difficulty. If *after* the deposit of the drop a little lycopodium be scattered over the surface, it is seen that a circular space surrounding the drop, of perhaps the size of a shilling, remains blank, and this however often the dusting be repeated, as long as any of the  $\text{CS}_2$  remains. The interpretation can hardly be doubtful. The bisulphide is really spreading all the while, but on account of its volatility is unable to reach any considerable distance. Immediately surrounding the drop there is a film moving outwards at a high speed, and this carries away almost instantaneously any dust that may fall upon it. The phenomenon above described requires that the water surface be clean. If a very little grease be present there is no outward flow, and dust remains undisturbed in the immediate neighbourhood of the drop. With the aid of the vertical lantern, and a shallow dish whose bottom is formed of plate glass, these experiments are easily shown to an audience.

#### *Movements of Dust.*

When dust of sulphur or lycopodium is scattered upon the surface of water contained in a partially filled vessel, it is found that after a few seconds the dust leaves the edge and that a clear ring is formed of perhaps a centimetre in width. Two explanations suggest themselves. The action may be due to grease communicated to the surface from the edge of the vessel; or, secondly, it may be the effect of gravity upon those particles of the dust which lie within the limits of the capillary meniscus. The first explanation is rendered improbable by the non-progressive, or at least but very slowly progressive, character of the effect; and it is negatived by a repetition of the experiment in a varied form. It is found that if the vessel, whether of glass or metal, be filled *over the brim*, so that the capillary meniscus is convex, then, although as before a bare margin is formed, the effect is due to a motion of the dust outwards (instead of inwards, as in the former case), and therefore not to be attributed to grease.

A similar movement of dust was to be observed in the experiment above recorded, where magnesia was scattered upon a pool of mercury, and is undoubtedly due to gravity; but the full explanation is not so simple as might appear at first sight.

Even in the interior parts of the surface at a distance from the edge the sulphur particles do not retain their initial positions, but form aggregations into which continually increasing numbers are attracted. This is also due to gravity, neighbours tending, as it were, to fall into the depression by which every particle is surrounded.

*Camphor Movements a Test of Surface-Tension.*

The theory of these movements, due to Van der Mensbrugghe, implies that they will take place with greater or less vigour so long as the tension of the surface, which may be in some degree contaminated, is greater than that of a saturated solution of camphor. If, however, the contamination be so great that the tension falls below this point, the solution of camphor can no longer spread upon the surface, and the movements cease. Thus, according to this theory and to observations\* upon a saturated solution of camphor, the movements are an indication that the actual tension does not fall below .71 of that of pure water.

Although there appeared to be no reason for distrusting this view, it was thought desirable to examine specially whether the cessation of the movements was really a question of surface-tension only, without regard to the character of the contamination. The readiest method of ensuring the equality of the tensions of two surfaces contaminated with different materials is to make the two surfaces parts of one surface, for two parts of the same surface cannot be at rest unless they have the same tension. The method of experiment was therefore to divide a surface of clean water contained in a large dish into two parts by a line of dust, and to communicate different kinds of grease to the surfaces on the two sides of the indicating line. If, for example, a small chip of wood, slightly greased with olive-oil, be allowed to touch one part of the surface, the line of dust is repelled by the expansion of that part, but the effect may be compensated by a slight greasing of the other part with oil of cassia. By careful alternate additions the line of dust may be kept central, while the two halves become increasingly greased with the two kinds of oil. At every stage of this process, so long as the surface is at rest, the tension of all parts is necessarily the same.

A large number of substances have thus been tried in pairs, of which may be mentioned oils of olive, cassia, turpentine, lavender, cinnamon, anise, petroleum, pseudocumene.

\* Phil. Mag. November 1890.



In no case could any difference be detected in the behaviour of camphor fragments on the two sides. Whenever possible, the quantities of oil were adjusted to the point at which the movements were just ceasing. In case of overshooting the mark, the excess of oil could be easily removed by strips of paper, partially immersed and then withdrawn, the action being equivalent to an expansion of the surface. In several cases the volatility of the substance with which the surface was contaminated led to a subsequent retraction of the line of dust. Thus freshly distilled oil of turpentine, even at first barely capable of arresting the movements, soon passes off.

As was shown by Tomlinson, oil of anise is incapable of arresting the camphor movements. In the experiment with a partition of dust, olive-oil will drive oil of anise into a very small space, whose area is doubtless dependent upon the amount of other impurities present. In this case, as in all others, the behaviour of camphor is the same on the various parts of the surface.

It may thus be taken as established that the relation of a contaminated surface to the camphor movements is one of surface-tension only.

A similar method of experimenting may be applied to a rough determination of the degree of purity of cleansed surfaces. The whole of the surface under test is lightly dusted over, and olive-oil is applied at several places close to the circumference until camphor movements are nearly arrested. After each addition of oil the dusted area contracts, and at the close of operations it gives a measure of the extent to which the original contamination must be concentrated in order to stop camphor.

A few numbers may be given as examples, although in all probability the result is influenced by a variety of circumstances. A circular area of 10 inches diameter, occupied by tap water, and cleansed by the flexible hoop described in former papers, was tested on July 28, 1891. The application of oil, just sufficient to stop the camphor movements, drove the dust into a central circular patch of  $2\frac{1}{2}$  inches diameter. When the surface was in its natural condition, unpurified by the action of the hoop, the central patch was of about 5 inches diameter. These numbers, approximately verified on repetition, show that the natural surface was about 4 times, and the purified about 16 times better than according to the camphor standard. The difference between the two cases is less than was expected, and would perhaps have been greater had distilled water been employed. It must be remembered also that contact with dust (sulphur) is unfavourable to the

purity of a water surface. In a very good light a special dusting might probably be dispensed with, the motion of the surface being evidenced by inevitable motes.

If the dust be applied in the first instance to a small central patch, which is then touched internally with a very small quantity of oil, the expansion of the dust in the form of a ring is followed by a slight but unmistakable rebound. The effect appears to take place when the surface is very clean to begin with, and is then somewhat difficult of explanation. I am disposed to think that it must be attributed in all cases to initial contamination. This is concentrated in front of the rapidly advancing ring, and has not time to diffuse itself equally over the whole external area. Under the influence of inertia the expansion of the central area may then proceed so far that its tension becomes greater than that of the parts immediately surrounding.

#### *Influence of Heat.*

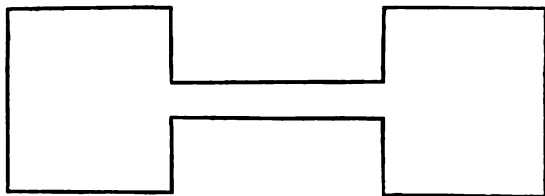
For a lecture experiment the effect of heat is best shown by holding a hot body near the surface of water contained in a shallow vessel with a glass bottom. The hot body may be the end of a glass rod heated by a flame, or more conveniently a small spiral of platinum wire, rendered incandescent at will by an electric current. The immediate effect of the heat is to lower the tension of the part of the surface affected; but the visible result depends entirely upon whether the surface be clean or otherwise. In the former case the heated surface expands, and an outward current is generated. This is rendered evident by the clearing away of dust. But if the original contamination exceed a very small quantity, a moderate expansion of the heated area brings the tension again up to equality with that of the surrounding surface, and there is no further action. In this case there is no visible clearing away of dust under the hot body.

Under favourable circumstances a very slight elevation of temperature suffices. On July 28 a shallow tin vessel 8×5 inches, the lid of a biscuit-box, was levelled and filled with tap-water from a rubber-hose, after a thorough preliminary rinsing *in situ*. A little dust (sulphur) was then scattered over, and the finger was brought underneath into contact with the bottom of the dish. After about 20 seconds the dust opened out, and a bare spot was formed over the finger of about  $1\frac{1}{2}$  inch diameter. A spirit-flame, applied for a few seconds under one end of the dish, cleared away the dust from the larger part of the area. If when quiet was nearly restored, a little fresh dust was applied, and the experiment with the

finger repeated, the effect was more pronounced than before, and the bared space much larger, showing that the treatment with the spirit-flame had driven away most of the residual contamination.

The best effects were obtained with a dish somewhat larger than that above mentioned ; and in subsequent experiments the difference of temperature between different parts was more readily maintained by the use of a vessel in which the main portions were connected by a comparatively narrow channel. In this way the tensions of surfaces, contaminated in different

Fig. 1.



degrees, may be equalized, the warmer purer surface in one compartment balancing the colder but greasier surface in the other. And the actual temperature difference necessary for equilibrium gives a measure of the small difference of tensions to be compensated\*.

When the surface of the liquid in the tin vessel is but very slightly greased, a spot can no longer be cleared by the warmth of the finger held underneath. Indeed the spirit-flame itself soon becomes ineffective. And yet the greasing may be so slight that camphor fragments move with apparently unabated vigour.

It is of interest to compare the behaviour of saturated solution of camphor with that of greasy water. The former can scarcely be brought to rest, unless covered up. This is doubtless due to evaporation of camphor, aided by local draughts. A spirit-flame drives away dust in a manner impossible in the case of a merely greasy surface, whose tension may nevertheless be decidedly higher than that of the camphorated water.

It may here be mentioned that the lowering of tension by camphor follows a different law from the lowering caused by soap. In the latter case the fall of tension requires time, and at the first moment of its formation a free surface has almost the tension of pure water. Similar experiments to those

\* The lowering of tension per degree Cent. is said to be  $\cdot 0018$  of the total value.

formerly recorded\* with soapy water have shown that the ratio of tensions for pure water and for solution of camphor are the same at the first moment of the formation of a free surface as when the measures are conducted statically.

### *Saponine and Soap.*

A strong infusion of horse-chestnuts allowed excellent bubbles to be blown, up to 4 inches or more in diameter. When the interiors of equal bubbles of soap and of saponine were brought into communication, the latter contracted and the former expanded, showing that the tension of the saponine film was the greater. In order to obtain equilibrium, the diameter of the saponine bubble required to be about half as great again as that of the soap bubble. These saponine bubbles exhibited the characteristic wrinkling, when caused suddenly to contract by withdrawal of part of the contained air.

The foaming of Highland waterfalls is doubtless attributable to dissolved vegetable matter. In the autumn of 1890 I had an excellent opportunity of observing these effects in the case of the river Creed at Stornoway. By the coalescence of smaller ones hemispherical bubbles of remarkable size, up to a foot or more in diameter, were frequently formed, and endured for a few seconds; and yet not the smallest bubble could be blown from a tobacco-pipe. However, by collecting some of the foam and allowing it to subside, which took a good while, I obtained liquid from which bubbles could be blown with a pipe up to 4 inches diameter. But these bubbles behaved like soap, and not as had been rather expected, like saponine, remaining perfectly light and smooth when the included air was rapidly withdrawn.

### *Separation of Motes.*

In the course of some experiments last year, in illustration of Sir G. Stokes's theory of ternary mixtures, I had prepared an association† of water, alcohol, and ether, in which the quantity of alcohol was so adjusted that the tendency to divide into two parts was almost lost. As it was, division took place after shaking into two nearly equal parts, and these parts were of almost identical composition. On placing the bottle containing the liquids in the concentrated light from an

\* Proc. Roy. Soc. March 1890.

† *Association* is here employed as a general term denoting the juxtaposition of two or more fluids. Whether the result is a *mixture* depends upon circumstances.

arc lamp, I was struck with the contrast between the appearance of the two parts. The lower, more aqueous, layer was charged with motes, while the upper, more etherial, layer was almost perfectly free from them. Some years ago I had attempted the elimination of motes by repeated distillation of liquid in vacuum, conducted without actual ebullition, but I had never witnessed as the result of this process anything so clear as the etherial mixture above described.

The observation with the ternary association, which happened to be the first examined, is interesting, because the approximate equality of the liquids suggests that the explanation has nothing directly to do with gravitation. But the presence of alcohol is not necessary. Ether and water alone shaken together exhibit the same phenomenon. It would appear that when the two liquids are mixed together in a finely divided condition, the motes attach themselves by preference to the more aqueous one, and thus when separation into two distinct layers follows, the motes are all to be found below.

An obvious explanation, which, however, stands in need of confirmation, is that under the play of the capillary forces the energy is least when the motes, which may be presumed to be denser than either liquid, are in contact with the denser rather than with the rarer of the two. The density here referred to is that which occurs in Laplace's theory of capillarity, and may need to be distinguished from ordinary mechanical density.

I have lately endeavoured to obtain some confirmation of the views above expressed by the use of other liquids. It would evidently be satisfactory to exhibit the selection of motes by the upper, instead of by the lower, layer. Experiments with bisulphide of carbon and water, and also associations of these two bodies with alcohol, which acts as a solvent to both, gave no definite result, perhaps in consequence of a tendency to the formation of a solid pellicle at the common surfaces. But with chloroform and water, and with associations of chloroform, water, and acetic acid (acting as a common solvent), the experiment succeeded. The motes were always collected in the *upper*, more aqueous, layer, even when the composition of the two layers into which the liquid separated was so nearly the same that a few additional drops of acetic acid sufficed to prevent separation altogether.

In this and similar cases a marked tendency to foaming may be observed when the composition is such that separation just fails to take place.

*The Lowering of Tension by the Condensation of Ether Vapour.*

The suspension of water in an inverted tube of small bore is familiar to all. The limit of diameter was investigated some years ago by Duprez\*. A glass tube, such as that shown in fig. 2, is ground true at the lower end, and at the upper end is connected to an india-rubber tube provided with a pinch-cock. Water is sucked up from a vessel of moderate size, the rubber is nipped, and by a *quick* motion the tube and the vessel are separated, preferably by a downward movement of the latter. In this way of working Duprez found that the liquid might remain suspended in tubes of diameter up to 16 millim., and with the aid of a sliding plate up to 19·85 millim. The theory is given in Maxwell's article in the *Encyclopædia Britannica* ("On Capillary Action"). For lecture purposes it is well not to attempt too much. The tube employed by me had an internal diameter of  $14\frac{1}{2}$  millim., and there was no difficulty in obtaining suspension. The experiment on the effect of ether-vapour was then as follows:—The inverted tube, with its suspended water, being held in a clamp, a beaker containing a few drops of ether was brought up from below until the free surface of the water was in contact with ether vapour. The lowering of tension, which follows the condensation of vapour, is then strikingly shown by the sudden precipitation of the water.

Fig. 2.

*Breath Figures and their Projection.*

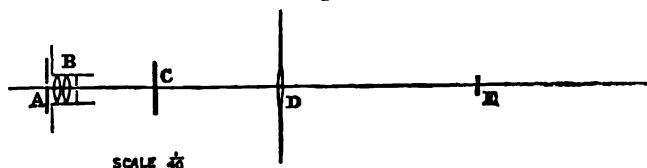
These figures are perhaps most readily prepared upon the plan described in Riess's 'Electricity.' The carefully cleaned glass plate upon which the image is to be received is placed upon a flat metallic slab, and upon it again rests the coin to be copied, for example, a shilling. The two conductors form the coatings of a Leyden jar, and are connected by wires to the discharging terminals of a large Wimshurst machine, the latter being set so as to give sparks about  $\frac{1}{4}$  inch long. In my experiments about 20 turns of the handle were found sufficient to impress the latent image.

\* "Sur un cas particulier de l'équilibre des liquides," *Bruxelles, Acad. Sci. Mém.* xxvi. 1851; xxviii. 1854.

The projection of the figures, developed upon the glass by breathing, requires a special arrangement, which it is the principal object of this note to describe. For this purpose the light simply transmitted by the undimmed parts of the plate must be intercepted, leaving the image to be formed by the light *diverted* from its path by the condensed breath. The arrangement was as follows:—

The ordinary condenser B (fig. 3) of the electric lantern was stopped down to an aperture of  $\frac{3}{4}$  inch, and provided a

Fig. 3.



somewhat divergent beam of light of corresponding diameter. At a distance of  $15\frac{1}{2}$  inches from the condenser was placed the slide C upon which a figure had been impressed. The focusing lens D was of plate-glass, 6 inches in diameter and 25 inches focus, and was of course distant from the breath figure by an amount slightly exceeding its own focal length. Any light that might pass outside was intercepted by a suitable mounting. So far there was nothing peculiar, except in respect to the dimensions of the focusing lens. But now between the latter and the screen was inserted a disk E of black card 2 inches in diameter, at such a distance (40 inches) from the lens as to receive a well-defined image of the hot carbons A. By this disk all regularly refracted light would be stopped, so that the screen would appear dark. If, however, any part of the prepared glass be dimmed by the breath, light is there diverted from its path, and thus escaping the stop proceeds to form an image of the part in question upon the screen. The dewed parts of the breath-figure are accordingly seen bright upon a dark ground; and with the arrangement described, in which the large diameter of the focusing lens is a leading feature, the projected images are very beautiful. A similar method would probably be adequate to the projection of smoke-jets.

In conclusion I may mention that the latent images can be developed in a more durable manner by a deposit of *silver*, the arrangements being such as are adopted for the silvering of mirrors, except that the action is stopped at an earlier stage. The washed and dried deposit may then be protected from mechanical injury by a coat of varnish.

March 4, 1892.

XLI. *Wave Propagation of Magnetism.*

By JOHN TROWBRIDGE\*.

VARIOUS attempts have been made to discover a wave-propagation of magnetism along bars of iron or around rings of this metal†. The ordinary method of investigation has been to subject the iron to alternating currents of a certain frequency, and to search for nodes along the extent of the bar or ring. The search has been conducted by employing small secondary coils of wire connected with a ballistic galvanometer or with telephones.

I have lately examined this question with a new instrument which I have termed a phasemeter, and which seems to me to be of great use in the subject of alternating currents. It consists of an application of Lissajous's method of studying the vibration of tuning-forks to two telephones which take the place of the tuning-forks. On the diaphragm of each telephone is affixed a mirror; and the axes of the telephones are so turned that the excursions of a spot of light, reflected from both the mirrors of the telephones, represent the figure produced by a combination of two motions at right angles to each other. In the telephone which I have employed, the diaphragms are about three inches in diameter, and are clamped delicately around the edges upon their support by little screw-clamps, which can be moved about until the diaphragm vibrates in unison with the alternating currents which are employed. Professor Eli W. Blake‡ has described a method of making the vibrations of a telephone-diaphragm visible. And since I began to work upon this subject M. Wien§ has described an instrument which he terms an optical telephone, which he employs for the measurement of alternating currents. In his method a stylus connected with the centre of the diaphragm touches a light mirror which is placed upon a flexible support, and thus the motions of the diaphragm are amplified. Great care must evidently be taken that the support of the mirror should move in unison with the stylus connected with the diaphragm. Professor Blake's method is an extremely sensitive one: for my purposes, however, I have found the method of clamping the diaphragm around its edges at suitable points sufficiently sensitive, and I

\* Communicated by the Author.

† Dr. Harold Whiting, *Proc. American Academy of Arts and Sciences*, p. 14 (1881); F. T. Trouton, '*Nature*,' November 1891.

‡ *American Journal of Science*, vol. xvi. (1878).

§ *Ann. der Physik und Chemie*, No. 12 (1891).



have not been troubled by the vibration of supports or disturbances in the room where the instrument was set up. The two telephones can be mounted upon the same support, and the entire instrument can be comprised in a box a foot square. I have used as a source of light a Welsbach burner, which consists of a fine gauze of zirconium placed in the flame of a Bunsen burner. A tin chimney provided with a circular opening of about  $\frac{1}{4}$  inch in diameter is placed over a glass chimney and a cylinder of writing-paper over the tin cylinder; a pinhole in the paper at the centre of the orifice in the tin chimney enables one to obtain a point of light on a light ground. This light ground diminishes diffraction-effects and enables one to see the cross wires of an observing-telescope or microscope. With a lime-light or electric light the difference of phase between branch circuits and main circuits through which alternating currents are pulsating can be shown to a large audience. On account of its application to the study of difference of phase in magnetic researches, I have termed the instrument a phasemeter. It is evident that it can be used to study the nodal lines of membranes and plates: for this purpose a plate or membrane provided with a mirror might be placed in front of a movable magnet containing at its end a coil of wire, and the vibrations of any membrane or thin plate could be compared with those of the diaphragm of a fixed and standard telephone.

I have also employed the instrument for studying differences in phase between branch circuits. That there are such differences of phase has been shown by Lord Rayleigh and others. This portion of my investigation I reserve for a subsequent paper.

The phasemeter permits of the study of the effect of different qualities of iron and steel in increasing the self-induction of, and therefore the impedance of, branch circuits; and it seems to me can be made of great use in the study of alternating-current motors. It is well known that two or three electro-dynamometers must be employed in the ordinary methods of determining change of phase. The phasemeter can be quickly employed and its adjustments are extremely simple. The application of this instrument to the question of magnetic waves is the subject of this paper. I have employed it both on rings and straight bars, laminated and solid. The ring I employed was 3 feet in diameter, and the diameter of its cross section was  $\frac{1}{4}$  inch. Two large coils of coarse wire were slipped upon the ring, through which an alternating current could be passed. These coils could be separated or joined together, and by a commutator opposite

poles or poles of the same name could be opposed. Two small coils of fine wire were also slipped upon the ring; each of these small coils was connected with a telephone. The diaphragm of one telephone gave a horizontal line of light, and the diaphragm of the other a vertical line, the combination of the two amplitudes giving a straight line, an ellipse, or a circle.

On placing one of the small coils at a fixed point on the ring on one side of one of the large coils and the other small coil between the two large coils, I examined the distribution of magnetism between the coils when the same poles or opposite poles were opposed to each other. A preliminary experiment in which the two small fine coils were on the same side of one of the large coils gave me no indication of nodes, or change of phase.

When, however, one coil was placed in the manner I have described between the two coils, and one on the opposite side of either of the coils, the following phenomena, which are sufficiently obvious, were observed. With a current of 2500 alternations per minute, an ellipse was seen in the phasemeter when the coils were at an equal distance from the ends of either of the large coils. When poles of the same name were opposed to each other, this ellipse changed from an ellipse with its major axis inclined to the right to an ellipse with this axis inclined to the left or the reverse, thus indicating a difference of phase of  $180^\circ$ .

At the central point on the iron between the two poles of the same name, the small coil placed there indicated no lines of force threaded through it, and consequently the telephone connected with this coil gave no amplitude, and a line of light either horizontal or vertical was given by the other telephone. When poles produced by the current in the large coils were of opposite sign, there was no appreciable change of phase produced by moving one of the small coils on the iron between these poles; only the amplitude of the diaphragm of the telephone connected with it changed.

The reason of the change of phase in the first case is obvious. In the case of two poles of the same sign which are opposed, the lines of force are threaded through the coil in one direction on one side of the middle point of the iron between the coils, and in the opposite direction on the other side of this middle point. With poles of opposite sign opposed, the lines of force are threaded in the same direction in whichever way the small coil is moved between these poles. The same phenomena can be observed on straight bars. An interesting manner of showing the change of phase produced

by the opposition of poles of the same or contrary sign, is to place one of the small coils on the core of a large coil, at one end of this latter coil, and to place the other small coil on a small rod of iron or steel, and to bring this rod with its coil near one end of the core of the large coil and afterwards to the other end. The change of phase of the ellipses is readily shown, and is evidently due to the threading of the lines of force by induction through the small coils in the same or in opposite directions.

If an incandescent lamp of about one-candle power is connected with one of the small coils, and the coil is placed on the iron ring between poles of the same name, the lamp will not glow; but on changing the poles so that two of opposite sign shall be opposed, the lamp immediately glows. This point, however, cannot be called a true nodal point, and I failed to find any other. Although it is probably true that the most distant molecule of the iron quivered under the periodic alternations of magnetism to which it was subjected, yet there was no wave-motion along the iron ring. Just as a distant molecule might have responded quickly to the first application of heat to the ring, there is no true wave-motion in the propagation of the heat. It seems to me that the propagation of magnetic disturbances produced by forced oscillations on iron bars is closely analogous to the propagation of heat over these bars, and that each molecule of the iron swings under the directive moment of the magnetic field somewhat like a pendulum in molasses.

Instead of the formula

$$\frac{d^2u}{dt^2} + k \frac{du}{dt} + n^2u = E \cos pt,$$

we have

$$\frac{d^2u}{dt^2} + k \frac{du}{dt} + n^2u = 0.$$

The curve of distribution of magnetism on the ring can be made to agree closely with an exponential form, which is evidently the solution of the second of the above equations.

The projection of the ellipses on a screen makes a very interesting lecture-experiment.

To ascertain whether changes of phase could be detected between the inner portions of a thick iron core subjected to alternating magnetic impulses and the outside of this core, I placed one of the coils of the phasemeter in a channel which was turned about the centre of a core of iron, the diameter of the curve being  $2\frac{1}{2}$  inches. Another coil with its centre

coinciding with the centre of the imbedded coil was slipped on the outside of the core: no changes of phase could be observed between the inner portions of the iron core and the outside portions. When an armature was placed over the imbedded coil, thus completely closing it in iron, hardly any lines of force were threaded through it. They were diverted to the surface of the iron core. Here we had the case of Thomson's marine galvanometer, and the amplitude shown by the telephone-diaphragm connected with the imbedded coil was reduced to almost nothing. When, however, the armature which extended over the entire cross section of the core was removed and an armature was employed which extended the iron which passed through the centre of the imbedded coil beyond the limits of the ends of the thick core, the lines of magnetic force were brought down from the surface of the iron and made to thread themselves through the imbedded coil. Properly chosen armatures can be made to closely resemble arrangements of lenses, bringing magnetic lines into bundles or spreading them. An incandescent lamp can thus be made to glow when it is connected with a coil imbedded in iron, by diverting the lines of magnetic induction through it with suitable armatures. To illustrate the distribution of the lines of force about an electromagnet, one can employ the phasemeter to advantage. By reducing the diameter of the iron ring on which the coils I have described are slipped, so that a sufficient number of lines of force are threaded from the north pole to the south pole of one of the large coils, one can show that an incandescent lamp can be lighted even when it is outside the coil in a plane perpendicular to the axis of one of the large coils and passing through its centre. It is evident that there would be no induction through the coil if the iron did not make a magnetic circuit.

The experiments I have described were conducted with an alternating machine giving currents of the period of 2500 to 5000 a minute. Doubling the rate of alternation only produced changes in amplitude.

Dr. Harold Whiting, in the paper I have cited, could find no true nodes in the propagation of magnetism along bars, and my instrument also shows none; and my conclusion is that which I have already given, namely that the propagation of magnetic induction in iron and steel is expressed by the equation of motion of molecular magnets in a resisting medium rather than by the equation of a wave-motion.

Jefferson Physical Laboratory,  
Cambridge, Mass., U.S.

XLII. *Note on the Selective Absorption of Light by Optical Glass and Calc-spar.* By EDWARD L. NICHOLS and BENJAMIN W. SNOW\*.

IN the course of some recent experiments †, the authors had occasion to measure the absorption which the rays from an incandescent lamp suffered in passing through a lens and a pair of Nicol's prisms. A number of observations upon the absorption of light by lenses have already been published, but they deal for the most part with the total absorption. Vierordt ‡, however, and very recently Kruess §, have measured the amount of absorption that takes place in each region of the visible spectrum, and Abney and Festing || have shown that such absorption may introduce very important errors into colour photometry.

For the details of the method by means of which the selective absorption in glass and calcite was determined, we must refer the reader to the article already cited. The lens and prism in question were mounted before the slit of a spectrophotometer under conditions which made it possible to compare the light from a glow lamp with rays from the same lamp after passage through the lens, or through both lens and prisms. In every other respect the two sets of rays under comparison were subjected to precisely the same treatment, in their path from the lamp to the eye of the observer. Any differences in the character of their spectra were ascribable, therefore, to losses incurred in traversing the lens, on the one hand, or to the combined action of the glass and the calcite on the other. No attempt was made to distinguish between losses due to absorption and those resulting from reflexion at the various surfaces.

In presenting our results, light of the region of the D line ( $\lambda=5890$ ) is taken as a standard of reference. The amount of light of this wave-length, transmitted by the lens, or by the Nicol's prisms, respectively, is taken as unity, and the relative proportions of light of other wave-lengths transmitted are given in terms of that quantity. This method expresses the character of the change. The results are

\* Communicated by the Authors.

† Phil. Mag., vol. xxxii. p. 406.

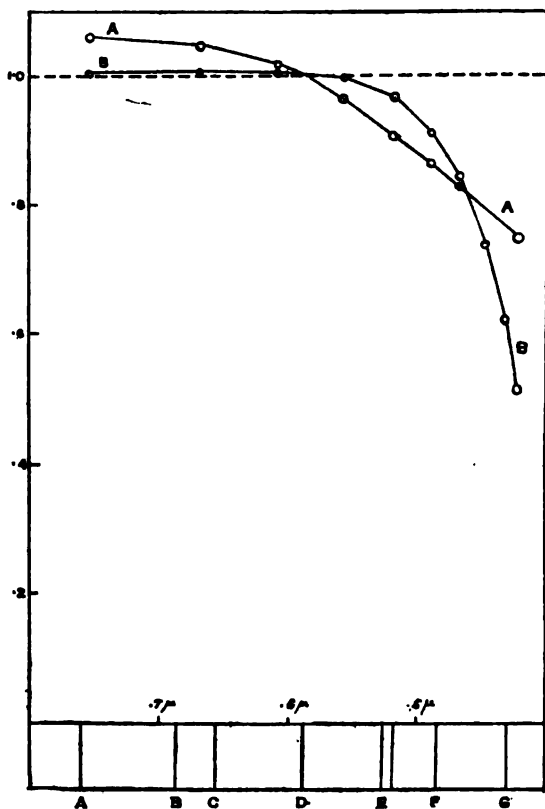
‡ *Die quantitative Spectralanalyse*, 1876, p. 113.

§ Gerhard und Hugo Kruess; *Kolorimetrie*, 1891, p. 252.

|| "Colour Photometry," 1888, *Philosophical Transactions*, vol. clxxix. p. 549.

merely relative. Expressed graphically, the curve of a substance the absorbing power of which is not selective is a horizontal line, with ordinate equal to unity.

Figure showing selective absorption :—(A) by a glass lens ;  
(B) by a pair of Nicol's prisms.



Tables I. and II. show the selective transmission in glass and calcite, respectively, expressed in the manner already indicated. Curves A and B of the accompanying figure present the data of the tables in graphic form. Abscissæ are wave-lengths and ordinates represent amounts of light transmitted.

TABLE I.

Selective transmission of light by a lens.

Wave-lengths.	Transparency for each wave-length in terms of that of the region of the D line.
$\lambda = .7530 \mu$	1.059
.6685	1.046
.6080	1.015
.5570	0.964
.5185	0.906
.4920	0.867
.4685	0.826
.4500	0.812
.4340	0.777
.4250	0.750

TABLE II.

Selective transmission of light by a pair of Nicol's prisms.

Wave-lengths.	Transparency for each wave-length in terms of that of the region of the D line.
$\lambda = .7530 \mu$	1.006
.6685	1.003
.6080	1.001
.5570	0.995
.5185	0.977
.4920	0.913
.4685	0.844
.4500	0.736
.4340	0.617
.4250	0.500

The lens referred to in Table I. is made of ordinary white crown glass (refractive index 1.549). It consists of two simple plano-convex lenses, the added mean thickness of the two being about 2 cm.

The Nicol's prisms were of the usual form, their thickness, measured in the direction of the path of the ray, being about 50 mm.

It will be seen that the glass of which the lens was constructed although not more strongly coloured than most optical glass, the tint being quite unnoticeable to the unaided eye, at least when seen through in the direction of the optical axis, is far from being colourless. The selective absorption begins to show itself in the red and the transparency falls off

steadily throughout the spectrum, the transparency for the region beyond the G line being only three fourths as great as that for red light.

In the case of the Nicol's prisms, however, the transparency throughout the red and yellow is quite uniform, diminishing less than one per cent. between the A line and the D line.

In the blue and violet, on the other hand, absorption appears to be relatively more marked in calcite than in glass.

Physical Laboratory of Cornell University,  
Ithaca, New York, June 1, 1891.

### XLIII. *Notices respecting New Books.*

*Guide through the Collection of Building-materials in the Imperial Natural-history Museum at Vienna.* [*Führer durch die Baumaterial-Sammlung, &c.*] By FELIX KABER. Small 8vo. 355 pages, with numerous plates. Lechner; Vienna.

DR. ARISTIDES BREZINA, Director of the Mineralogical Department of the Museum, gives a short Preface, noticing the history of this special collection, giving due credit to those who have helped in the work, and especially acknowledging the industry and acumen of F. KABER in perfecting this extensive and useful Collection. An Introduction gives (1st) a general account of the collection and of the method followed in its arrangement and in the Guide-book: (2nd) brief notices of the characteristics of the most common and useful rock-materials: (3rd) the geological order of the rocks and strata: (4th) a Bibliography of memoirs and books on constructive materials, in chronological order from 1831.

In the body of the work the main arrangement is geographical; and a city or town in each division, in many cases supplying one or more chief buildings (of which there are forty "phototypes"), has a detailed account of the nature and sources of the various building-materials used in these constructions; and its paving-stones and road-metal are also carefully noted. Thus Vienna, Linz, Salzburg, Innsbruck, Bregenz, Graz, Klagenfurt, Laibach, Görz, Trieste, Parenzo, Zara, Prague, Brünn, Troppau, Lemberg, Cracow, Czernowitz, Budapest, Hermannstadt, Klausenberg, and Agram, give full opportunities for detailing the particulars of the building-stones, decorative stones, sand, lime, hydraulic cement, plaster, bricks, roofing-stone, &c., locally used in Austria-Hungary. Of foreign countries large and well-known buildings at Cologne, Regensburg, Strassburg, Nürnberg, Dresden, Rome, Milan, Paris, Brussels, and Schaerbeck are illustrated; and the materials used in them and in other buildings, as well as in streets and roads, are enumerated according to the many examples in the Museum. Shorter, but useful, notices of the building-materials in the Museum from England, Norway, Russia, Switzerland, Spain, Portugal,



Greece, United States of America, some parts of Asia, Algeria, Tunis, and Egypt are also given.

This work is an excellent model for what might be done with advantage by geologists and architects in other countries: indeed Dr. Karrer intimates that England in particular could produce, and decidedly requires, such a Guide-book, having reference to the local museums, quarries, and great buildings, whether public or private works.

The exquisitely neat and truthful reproductions of the many architectural photographs used in illustrating this Guide-book greatly enhance its value both for the general reader and the connoisseur of stone-work. A long list of corrections is supplied; and a very full and useful Index of things, places, and names occupies the last fifty pages.

*Dynamics of Rotation.* By A. M. WORTHINGTON, M.A., F.R.A.S.  
London: Longmans, 1892.

IN the ordinary text-books of Elementary Mechanics and Dynamics of a Particle the subject of rotational motion is, as a rule, treated with extreme brevity, and is sometimes entirely neglected. Consequently a student who has made himself quite conversant with the principal facts relating to motion of translation often meets with great difficulties on commencing a course of Rigid Dynamics, arising mainly from his want of familiarity with the properties of couples and the phenomena presented by a spinning body. In addition to this the examples and problems in treatises on Rigid Dynamics usually involve motion in three dimensions, and a knowledge of solid geometry is required for their solution. The aim of the present book is to introduce the student a little more gradually into the intricacies of the subject of rotation, by confining his attention at first to problems involving motion about a single fixed axis. The laws of such motion lead up to the definition of a moment of inertia, and a considerable portion of the book is devoted to the methods of finding moments of inertia and the various theorems respecting them. The subject of oscillations then comes in for a share of attention, after which the laws of conservation of angular momentum and of the independence of translation and rotation are enunciated and applied. The book concludes with an interesting chapter on the phenomena of precession. The aim of the author has been throughout to treat the subject from a physical rather than a mathematical standpoint; and wherever possible he has appealed to experiment to illustrate and confirm the mathematical investigations. We learn from the preface that the book is intended for those students of Engineering or Physics who have not a sufficient knowledge of mathematics to enable them to follow the works of mathematical writers on Rigid Dynamics. For such it should prove useful, but it will be of some service also to the mathematical reader, by giving him clearer ideas as to the physical meaning of the equations which he uses.

JAMES L. HOWARD.

XLIV. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

[Continued from p. 152.]

December 9, 1891.—Sir Archibald Geikie, D.Sc., LL.D., F.R.S.,  
President, in the Chair.

**T**HE following communications were read :—

1. "On the Rocks mapped as Cambrian in Caernarvonshire." By the Rev. J. F. Blake, M.A., F.G.S.

In this paper the following is given as a definite succession in the Cambrian series:—1. Pale Slates; 2. Upper Purple Slates; 3. St. Ann's Grit; 4. Lower Purple Slates; 5. Rhiw-wn Grit; 6. Hard banded Pale Slates and Hällefintas; 7. Bangor Conglomerate; 8. Hard banded Pale Slates and Hällefintas; 9. Bangor Breccia; 10. Blue banded laminated Grits; 11. Tairffynnon Conglomerate; 12. Blue banded laminated Grits; 13. Brithdir quartz-felsite Grit.

The general succession is argued to be the same in the isolated portion east and south of Bangor as in the main mass. The existence or otherwise of a base on the mainland is considered to depend on the age assigned to the Dinorwic felsite, and the presence of the summit-beds to depend on whether the Bronllwyd Grit (stated to belong to the overlying group) rests conformably or unconformably on the Cambrian rocks.

It is argued that the rocks to the west of the Llyn Padarn felsite belong to the lower part of the series and those to the east to the upper, and that the felsite is a volcanic complex belonging to the middle of the Cambrian period.

A post-Cambrian age is assigned to the conglomerates of Moel Tryfan and Llyn Padarn, thus causing the break at the base of the Silurian system to assume an increased importance.

2. "The Subterranean Denudation of the Glacial Drift, a probable cause of submerged Peat and Forest-beds." By W. Shone, Esq., F.G.S.

A description is given of a section at Upton, Chester, where Boulder Clay rests upon "mid-glacial sands." The Boulder Clay sinks to a lower level in the small valleys which are cut through into the sands; and the author supposes that this is due to the subterranean denudation of the sands, which would be greatest near the valleys, and become less at a distance from them. He considers such denudation is capable of producing submerged peat and forest-beds, and accounts for the splitting of peat-beds, as described by Mr. G. H. Morton, by a somewhat similar action, which he believes may have also operated in Carboniferous times, causing the splitting of coal-seams.

3. "High-Level Glacial Gravels, Gloppa, Cynr-y-bwch, near Oswestry." By A. C. Nicholson, Esq. Communicated by W. Shone, Esq., F.G.S.

These gravels are found at Gloppa, and are situated at a height of from 900 to 1160 feet above sea-level, on the eastern slope of a ridge of Millstone Grit which forms the western border of the Cheshire and Shropshire plain.

The beds present the appearance of having been abruptly cut off on the north-eastern slope. The gravels are in places much contorted, and false-bedding is frequent. They contain numerous striated erratics. Amongst the boulders are Silurian grits and argillites, granites like those of Eskdale, Criffel, &c., Carboniferous rocks, Lias shale, and Chalk flints. The shells are often broken, rolled, and striated, but the bulk of them are in fairly good condition.

A list of the shells is given, including nine Arctic and Scandinavian forms not now living in British Seas, nine northern types, also found in British seas, two southern types, and nearly fifty species of ordinary British forms. Comparative lists of the shells of Moel Tryfan and of those now living in Liverpool Bay are placed side by side with the list of shells from Gloppa.

December 23.—W. H. Hudleston, Esq., M.A., F.R.S.,  
Vice-President, in the Chair.

The following communications were read :—

1. "On Part of the Pelvis of *Polacanthus*." By R. Lydekker, Esq., B.A., F.G.S.

2. "On the Gravels on the South of the Thames from Guildford to Newbury." By Horace W. Monckton, Esq., F.G.S.

The author stated that the greater part of the hill-gravel in the district referred to belonged to the Southern Drift of Prof. Prestwich, and that the valley-gravels for the most part consisted of material derived from the Southern Drift. Small patches of Westleton Shingle and Glacial Gravel occurred near Reading and Twyford.

He divided the Southern Drift into three classes :—

1. Upper Hale type, characterized by the abundance of small quartz pebbles and the scarcity of chert.

2. Chobham Ridges type, with abundance both of small quartz pebbles and chert.

3. Silchester type; quartz scarce, and chert very rare or altogether absent.

He described the localities at which these types occurred and their limits of distribution, and then referred to the Glacial Gravels of the Tilehurst plateau, which he believed to have been deposited before the excavation of the valley of the Thames between Reading and Goring.

The author then dealt with the valley-gravels, which he believed to be mainly derived from the hill-gravels of the immediate neighbourhood, and showed how the various types of hill-gravel had

contributed materials for the valley-gravels. He explained that, with the possible exception of the Westleton Shingle, he entirely rejected the theory of marine action in connexion with the formation of these gravels, and thought that the Glacial Gravels were probably for the most part due to floods during melting of large quantities of ice. The remaining gravels, he believed, had been spread out by water in valleys; as denudation proceeded, the gravel, by protecting the ground upon which it lay, came to stand out as the capping of the plateaux and hills; as the gravel itself was denuded, the materials were carried to lower levels, forming new gravels; and this process has been repeated up to the present time. He explained that Prof. Rupert Jones and Dr. Irving had already adopted this theory in part, but that he differed from them in the entire exclusion of marine action.

3. "The Bagshot Beds of Bagshot Heath." By Horace W. Monckton, Esq., F.G.S.

The author stated that certain changes in the classification of the Bagshot Beds had recently been proposed, and he gave reasons for preferring that at present in use, which was originally proposed by Prof. Prestwich in 1847, viz. a threefold division into Upper, Middle, and Lower Bagshot.

He then argued against the theory that the Upper and Middle Bagshot Beds overlap the Lower Bagshot on the north-western side of the Bagshot district, as had been suggested by Dr. A. Irving; and, dealing with the various localities where Upper Bagshot had been alleged to exist resting on Lower Bagshot or on London Clay, he contended that in every case the evidence in favour of Upper Bagshot age broke down on examination.

January 6, 1892.—W. H. Hudleston, Esq., M.A., F.R.S.,  
Vice-President, in the Chair.

The following communications were read:—

1. "On a new Form of *Agelacrinites* (*Lepidodiscus Milleri*, n. sp.) from the Lower Carboniferous Limestone of Cumberland." By G. Sharman, Esq., and E. T. Newton, Esq., F.G.S.

2. "The Geology of Barbados.—Part II. The Oceanic Deposits." By A. J. Jukes-Browne, Esq., B.A., F.G.S., and Prof. J. B. Harrison, M.A., F.G.S.

The Oceanic deposits rest unconformably on the Scotland Series, with which they contrast strongly in every respect. They are divisible into five portions:—

1. Grey and buff calcareous marls (Foraminiferal).
2. Fine-grained red and yellow argillaceous earths.
3. Pulverulent chalky earths (Foraminiferal).
4. Siliceous earths (Radiolarian).
5. Calcareo-siliceous and chalky earths (Foraminiferal).

The whole series is more calcareous in the northern than in the

southern part of the island, and layers of volcanic dust occur in it at various horizons. There is everywhere a passage from the more siliceous to the more calcareous earths.

From the palæontological and lithological evidence the authors conclude that the depth of water in which the Oceanic beds were deposited varied between 1000 and 2500 fathoms. The microscopical and chemical evidence shows that the Radiolarian earths are similar to modern Radiolarian ooze; that the calcareo-siliceous earths are similar to what is called by Prof. Haeckel "mixed Radiolarian ooze"; that some of the Foraminiferal earths are comparable to *Globigerina*-ooze from 1000 fathoms, and that others greatly resemble European Chalk; and, finally, that the coloured clays bear a strong resemblance to the so-called "red clays" of modern oceanic areas. Hence the raised Oceanic deposits of Barbados seem to present us with an epitome of the various kinds of deposits which are found on the floors of warm seas at the present day. Equivalent deposits are known in Trinidad and Jamaica; and it is inferred by the authors that the whole Central American and Caribbean region was deeply submerged during the Pliocene period, leaving free communication at that time between the Atlantic and Pacific Oceans.

An Appendix by Mr. W. Hill treats of the minute structure of the Oceanic earths and limestones and of the Foraminiferal muds and detrital earths; and this is supplemented by a Report from Miss Raisin on the inorganic material of certain Barbados rocks.

3. "*Archæopneustes abruptus*, a new Genus and Species of Echinoid from the Oceanic Series in Barbados." By J. W. Gregory, Esq., B.Sc., F.G.S.

#### XLV. Intelligence and Miscellaneous Articles.

ON THE INTENSITY OF THE RADIATION OF GAS UNDER THE INFLUENCE OF THE ELECTRICAL DISCHARGE. PRELIMINARY NOTICE BY K. ÅNGSTRÖM\*.

I. **T**HE interesting phenomena which accompany electrical discharge through rarefied gases, although still for the most part unexplained, have of late been repeatedly investigated both in the optical and in the electrical direction. The quantitative relation between the optical and the electrical phenomena has, however, been but little studied. Now it is only by a more perfect knowledge of this relationship that we may hope to understand and explain the origin and the nature of the radiation which we observe in Geissler's tubes, as also the part which electricity plays in those remarkable phenomena.

Calorimetrical researches on the development of heat in Geissler's

\* Translated from a separate impression communicated by the Author.

tubes have been made by E. Wiedemann (*Wied. Annalen*, vol. vi. p. 298, 1879, and vol. x. p. 202, 1880), and by M. Nasselberg (*Mém. de l'Acad. Imp. des sciences de St. Pétersbourg*, vol. vi. No. 1, 1879). M. G. Staub further has recently (*Inaugural dissertation*, 2nd part, Zurich, 1890) made some experiments on the development of heat in the discharge of Leyden jars through Geissler's tubes filled with air and hydrogen: he has at the same time attempted to determine the ratio of the obscure to the luminous radiation. With this view he enclosed the tube in a Bunsen's ice-calorimeter, where the tube and the calorimeter successively transmitted or absorbed the luminous radiation; in the latter case the tube was blackened.

Not only the total energy absorbed by the gas and that radiated have been measured in these experiments, but also the energy received directly from the sides of the tubes, and which they changed into heat. However valuable these researches may have been, they do not give a direct answer to the question of the radiation of the gas under the action of the electric discharge. A direct determination of this intensity has not yet been made so far as I know, and the possibility of such a determination, with our present resources, has even been questioned. For this reason I have endeavoured to use the bolometer to determine the radiation of different gases under the action of the electrical current; to express the intensity of this radiation in absolute measure; and to endeavour then to determine the relation of the radiation to the causes which produce it.

After having worked for more than a year at this very arduous investigation, I think I may consider that the preliminary trial experiments are completed. I shall explain here some of the results at which I have arrived; treating afterwards with greater detail the materials which I have collected.

II. As the light of the kathode is too feeble and its shape too variable to justify the hope that I could obtain very accurate quantitative results, I restricted myself to the investigation of the positive light only.

I used cylindrical glass tubes of the same thickness and 10 to 15 mm. in diameter. The electrodes were usually placed in side tubes at right angles with the principal tube. One end of the tube and sometimes both were closed by a smooth plate of rock-salt fixed hermetically by means of silicate of soda. In the prolongation of the axis of the tube a sensitive bolometer was placed, separated from the tube by a double screen with apertures in the direction of the axis of the tube. Between the sides of the screen was another double movable screen.

The indications of the bolometer were compared with one of my instruments for determining radiant heat in absolute measure (*Acta Reg. Soc. Upsal.* series iii. 1886. See also *Öfversigt af Kongl. Vet.-Akad. Förhandl.* No. 6, p. 379, 1888). I found in this way that one division of the scale corresponded to a radiation of  $278 \times 10^{-9}$  gramme calories per second and square centimetre.

To ascertain if and how far the character of the radiation changes with the different conditions of the gas, I measured on the one hand the total radiation, and on the other the radiation transmitted by a plate of alum of 3.95 mm. in thickness. The radiation determined by direct observations consists of two parts—the radiation of the gas, and that of the more or less heated sides of the tube. The latter part must be eliminated, which is effected by a series of observations of the radiation of the tube after the current has been opened. From the curve of radiation thus found it is easy to calculate the radiation of the tube during the experiment, and by subtracting this quantity from the quantity observed during the passage of the current the radiation of the gas is obtained. This value, however, is increased by the reflexion of the sides of the discharge-tube, and diminished on the other hand by the reflexion of the plate of rock-salt which closes the tube. Direct experiments, the details of which I suppress, have enabled me to make a satisfactory correction for this reflexion, and therefore to determine the total radiation in absolute measure.

As source of electricity I principally used an accumulator of 800 elements of Planté's pattern, and also a Ruhmkorff's coil of medium size. The current was determined by a dead-beat reflecting-galvanometer, with a wire insulated by caoutchouc. The difference of potential between two points in the positive light was measured by means of two thin platinum wires, soldered in the discharge-tube, and connected with a Mascart's quadrant-electrometer. For exhausting the tube I used, in my later experiments, a pump on Sprengel's principle, modified by Prytz (*Wiedemann's Annalen*), and further improved by myself.

I have spared no pains to make the gases as pure as possible. Thus neither stopcocks, nor caoutchouc tubes, nor grease were used either in the preparation of the gas or in the connexion of the tube with the air-pump. To introduce the gases into the discharge-tube, to dry them, and to prevent the access of mercurial vapour to the tube, I used the method of M. Cornu (*Journal de Physique*), slightly modified for my purpose. My researches extended to oxygen and hydrogen liberated by electrolysis of pure water acidulated by phosphoric acid; to nitrogen produced by leading pure air freed from carbonic acid over heated copper (first reduced by hydrogen); and to carbonic acid produced by heating sulphuric and oxalic acids and purified by passing through a solution of potash.

III. I give here the most important results of this research.

1. *For a given pressure, the radiation of positive light is proportional to the intensity of the principal current.* It is true that on using very powerful currents small divergences are observed, but in this case they are always accompanied by a permanent alteration of the gas, so that the same radiation is not met with again for less strong currents.

2. If the electric current is kept constant and the pressure is varied, it appears that *the intensity of total radiation scarcely varies*

between the limits 0.1 to 1.5 mm., but it increases a little at higher pressures. At pressures exceeding 1.5 mm. the character of the discharge seems to be modified, after which the radiation increases considerably with the pressure after having passed, at any rate in certain cases, through a minimum.

3. For the same gas under the same pressure the composition of the radiation is constant, and does not depend on the intensity of the electrical current. This is subject to the reserve stated in (1).

4. When the density of the gas changes the composition of the radiation changes also, in so far that the ratio of the intensity of radiation of the shorter wave-lengths to that of the total radiation decreases with increase of pressure.

This ratio, indicated in my experiments by the ratio of the radiation transmitted by a plate of alum to that of the total radiation, varies for instance between the pressures 0.1-1.6 mm., for carbon dioxide from 46 to 15 per cent., and for nitrogen from 94 to 60 per cent.

5. It will be seen from these figures that the ratio between the luminous and the total radiation rises to considerable values for very low pressures, values far greater than those of our ordinary luminous sources. This ratio, however, does not always attain such high values in the electrical discharge in rarefied gases. At pressures of 5-10 mm. it is rather small.

6. The intensity of the total radiation varies greatly for different gases. It is not in a simple ratio with the molecular weight of the substance, or with the difference of potential in the layer of radiating gas. It does not appear to depend essentially on the absorption of the gas at the ordinary pressures and temperatures, either as regards its intensity or in reference to its composition, as can be seen by the following table, which contains values for the radiation and the difference of potential for a pressure of 0.7 mm. and for the same strength of the electrical current.

	Total.	Radiation transmitted by alum.	Difference of potential.
Oxygen .....	1.0	.....	17
Hydrogen .....	5.9	2.2	19
Nitrogen .....	30.0	2.4	25
Carbon dioxide.....	13.6	3.8	27

IV. In the case of low pressures it appears to me that we may give the following explanation of these phenomena.

When the rarefied gas becomes a conductor of an electrical current, it is the molecules principally which serve to transport electricity, that is to say the active molecules which radiate. The



number of these molecules is proportional to the intensity of the current, and varies but little with the variations of pressure as long as the discharge retains its character (III. 1 and 2). This radiation is of an irregular character according to M. R. von Helmholtz (*Die Licht und Wärmestrahlung verbrennender Gase*, Berlin 1890); or it belongs to the class of phenomena to which M. E. Wiedemann (*Wied. Ann.* xxxvii. p. 177, 1889) has given the name of *phenomena of luminescence* in this sense, that the composition of the radiation does not correspond with the temperature of the gas. The radiation may be of extreme intensity in the groups of short wave-lengths.

When the pressure increases and with it the number of inactive molecules, the irregular radiation of the active molecules may more easily be transmitted to the former. The number of radiating molecules increases therefore, and consequently also the radiation of the gas, but it changes in character in this sense, that the radiation of the groups of shorter wave-lengths relatively diminishes.—*Öfversigt af Kongl. Akad. Förhandl.*, 1891, No. 6.

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#### ON THE REPULSIVE FORCE OF RADIATING BODIES.

BY PETER LEBEDEV.

It was shown by Maxwell\* that a pressure is exerted on absorptive bodies by incident rays in the direction of their propagations, and that this can be expressed in the form

$$P = \frac{E}{v}, \quad . . . . . (1)$$

in which  $E$  is the energy imparted to the body by the incident rays in unit time, and  $v$  the velocity of light in the medium in which the body is placed.

Independently of Maxwell, Bartoli† and Boltzmann‡ arrived at analogous results in treating the case of reflexion. Bartoli found that at perpendicular incidence the rays exert a pressure against a mirror, which is twice as much as that which, according to Maxwell, they would exert against an absorbent body.

In what follows the ratio of the repulsion produced by radiation to the Newtonian attraction is deduced both for our sun, and for a hot spherical body in general. The expressions obtained hold only for absolutely black bodies, whose dimensions are great in comparison with the wave-length of the incident radiation; accordingly the interesting questions respecting the repulsive force in the tails of comets, and the mutual action of two adjacent molecules in the body cannot be solved, but only indicated. . . .

As it is only the order of the magnitude of the desired ratio

\* Electricity and Magnetism, § 792.

† Exner's *Repertorium*, vol. xxi. p. 198 (1885).

‡ *Wied. Ann.* vol. xxii. p. 31 (1884).

which is of interest, the simplest case only shall be treated here; the body attracted is assumed to be spherical, to absorb the whole of the energy which falls upon it, and to radiate it then uniformly in all directions; the numerical calculations will be made with great allowances.

Assuming with Langley as the value of the solar constant, that is the quantity of heat which falls perpendicularly in a minute on 1 square centimetre,  $C=3$  gramme-calories, and the mechanical equivalent of heat  $B=425$  gramme-metres, the quantity of energy  $E$  which falls in a second on a square centimetre will be

$$E = \frac{c}{60} B = 21 \text{ gramme-metres.}$$

Taking the velocity of light  $V=3 \cdot 10^8$  metres, we can from (1) calculate the pressure  $P$  which a pencil of rays of 1 sq. cm. section exerts on an absorbing body at the distance of the earth

$$P = \frac{E}{V} = \frac{2}{3} 10^{-7} g^* ;$$

or in absolute units

$$P = 0.6 \times 10^{-4} \text{ dynes.} \quad (2)$$

If we take the earth's distance from the sun  $\rho = 15 \cdot 10^{12}$  cm., and the velocity of the earth's path  $\sigma = 3 \cdot 10^6$  cm., the sun's acceleration

$$a = \frac{\sigma^2}{\rho} = 0.6 \text{ cm.}$$

Accordingly the sun attracts 1 gramme mass, at the earth's distance, with the force  $A$ ,

$$A = 0.6 \text{ dyne.} \quad (3)$$

The action which the sun exerts on a body which rotates around it, consists on the one hand in the Newtonian attraction, and on the other hand in repulsion from radiation. Given a spherical body at the earth's distance, which absorbs the whole of the solar energy which falls upon it, and then radiates it uniformly in all directions; if  $r$  is its radius in centimetres, and  $\delta$  its density in reference to water, we can calculate both the force  $G$  with which it is attracted, and the force  $H$  with which it is repelled:

$$G = \frac{4}{3} \pi r^3 \delta A,$$

$$H = \pi r^2 P.$$

From this we can calculate the resultant force  $F$ , and express it in fractions of the force of gravitation with which the body is attracted by the sun:

$$F = \frac{G-H}{G} = 1 - \frac{H}{G} = 1 - \frac{3P}{4A\delta} \quad (4)$$

\* The pressure of a pencil of rays of 1 square metre section amounts to  $\frac{1}{3}$  mg.

For the body in question  $F$  represents a characteristic constant, which is independent of the distance from the sun, since  $P$  and  $A$  depend in the same way on this distance.

Replacing  $P$  and  $A$  in (4) by their numerical magnitudes (2) and (3), we obtain approximately

$$F = 1 - \frac{10^{-4}}{r\delta} \dots \dots \dots (5)$$

It is clear from this that for all bodies in which  $\delta > 1$  and  $r > 10$  m., the deviations from Newton's law must lie below the errors of observation of the most accurate measurements.

The smaller  $r$  is chosen, the more prominent does the repulsive force of the sun become. If we pass over to comets' tails, which are known to consist principally of gaseous hydrocarbons\*, they represent for us the individual molecules in which, according to Exner†,  $\delta < 10$  and  $r < 10^{-8}$  cm. Our formula (5) cannot be in strictness applied to this case, since the individual molecules are not absolutely black bodies, and their radii are very small compared with the wave-length of the incident radiation; formula (5), however, allows us to suppose that in this case the repulsive force may be several times greater than the attractive, that this may be of different magnitudes for different vapours, and decreases in inverse proportion to the square of the distance from the sun. Bredichin‡ has calculated from the curvatures of the tails of forty comets, by Bessel's method, the repulsive force which the sun exerts on various substances forming the tails, and has found three values 17.5, 1.1, and 0.2; these values can without straining be referred to the mechanical action of the radiation, without, like Zöllner§, having recourse to the assumption of an electrostatic charge on the sun.

It may be observed that Faye|| has already expressed the opinion that the repulsive force of the sun is to be sought in its radiation.

We now turn to general considerations: any body, the temperature of which is different from the absolute null point, radiates and exerts on an adjacent body a repulsion by radiation besides the Newtonian attraction.

If, in place of the sun, we have a spherical body the radius of which is  $R$  centimetres, and the density  $\Delta$ , and if 1 square centimetre of its surface radiates  $Q$  gramme-calories in one second, we can treat this case based on the results found for the sun, taking into consideration that

\* Scheiner, *Spectralanalyse der Gestirne*, pt. iii. chapter 3; Leipzig, 1890.

† Wied. *Beiblätter*, vol. ix. p. 714 (1885).

‡ *Révision des valeurs numériques de la force répulsive*; Leipzig, 1885.

§ *Ueber die Natur der Kometen*; Leipzig, 1872.

|| *Compt. rend.* vol. xciii. pp. 11 and 362 (1881).

the sun's radius . . . . .  $R_0 = 7 \cdot 10^{10}$  cm.  
 „ „ density . . . . .  $\Delta_0 = 1.4$ .  
 „ radiation of 1 square cm. of  
 its surface in 1 second . . .  $Q_0 = 2000$  gramme-calories\*.

If we denote by  $s$  the ratio of the repulsive force of the radiation to the Newtonian force of attraction, we may contend that  $s$  is directly proportional to  $Q$ , inversely proportional to  $\Delta$  and also to  $R$ †.

For the sun we have from (5) the value  $s_0$ :

$$s_0 = \frac{10^{-4}}{r\delta}$$

Hence for any other body we have

$$s = s_0 \frac{Q}{Q_0} \frac{\Delta_0}{\Delta} \frac{R_0}{R}; \dots \dots \dots (6)$$

or, replacing the magnitudes  $s_0$ ,  $Q_0$ ,  $\Delta_0$ , and  $R_0$  by the corresponding numerical values, we obtain approximately

$$s = 5 \frac{Q}{r\delta R \Delta} \cdot 10^3. \dots \dots \dots (7)$$

The resultant  $K$  of the attraction and repulsion is

$$K = 1 - s = 1 - 5 \frac{Q}{r\delta R \Delta} \cdot 10^3. \dots \dots \dots (8)$$

Christiansen ‡ found for a black body that radiates  $Q'$  gramme-calories in a second at  $0^\circ$  C. from 1 sq. centimetre of its surface, approximately

$$Q' = (1.21 \cdot 10^{-12}) (274)^4 = 0.004 \text{ gramme-calorie.}$$

Hence the force  $K'$  with which a spherical absolutely black body, whose radius is  $R$  cm., density  $\Delta$ , and temperature  $0^\circ$ , attracts another spherical body in space whose radius is  $r$  cm. and density  $\delta$ , is furnished by the expression

$$K' = 1 - \frac{20}{r\delta R \Delta} \cdot \dots \dots \dots (9)$$

Accordingly, two bodies whose temperatures are  $0^\circ$ , radii  $R=r=2$  mm., and densities  $\Delta=\delta=10$ , would neither attract nor repel each other in space. If we assume that the radii of the bodies

\* If at the distance of the earth  $\rho = 15 \cdot 10^{12}$  centim. the quantity of heat  $c/60 = 0.05$  gramme-calorie falls on 1 square centim., then 1 square centim. of the sun's surface, which is at a distance of  $R_0 = 7 \cdot 10^{10}$  centim. from the centre, radiates the quantity of heat  $Q_0 = 0.05 (\rho/R_0)^2 = 2000$  gramme-calories in one second.

† Since the attractive force of the mass is proportional to  $R^3$ , and the repulsive force of radiation to  $R^2$ .

‡ Wied. Ann. vol. xix. p. 272 (1893).

are still smaller, we see that the repulsion with them would be considerably greater than the attraction; hence particles of dust whose radii are smaller than the thousandth of a millimetre would repel, at a temperature of  $0^{\circ}$  in space, with a force the order of whose magnitude is a million times greater than that of the Newtonian attraction.

If we take the radii still smaller, we come gradually to molecular dimensions. Our formula (8) is, however, no longer applicable to individual molecules, since they are not perfectly black, and both their dimensions and their respective distances in bodies are small compared with the wave-length of the radiation; the action of two molecules on each other must therefore, like that of two resonators, be treated in a complex manner.

If equation (8) does not give us the direct action of two molecules, it reminds us that in investigations of the nature of what are called "molecular forces" we cannot, without more ado, neglect the forces arising from the reciprocal radiation of the molecules, without having first defined what fractions of the molecular forces they form.—Wiedemann's *Annalen*, No. 2, 1892.

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#### AN ELECTROLYTIC EXPERIMENT. BY LEO ARONS.

If a copper cylinder is placed in an electrolytic cell which contains copper-sulphate solution between two copper electrodes, part of the current sent through the cell will disperse in the cylinder. In the places at which the lines of flow enter the cylinder copper is deposited, while an equivalent quantity is dissolved at the places where they emerge. If the copper cylinder is arranged so that it rotates easily about a horizontal axis, it will begin to rotate as soon as the current is closed, since the part opposite the anode is heavier, the other lighter. As the conductivity of the copper so greatly exceeds that of the liquid, we can use a hollow cylinder without any material diminution in the number of lines of flow which pass through the metal. From this circumstance a considerable mobility of the cylinder can be attained, even when the bearings of the axle are very roughly worked. The thickness of the hollow cylinder can be easily so calculated that the cylinder, which is closed at the ends, floats in a concentrated solution of copper sulphate, but sinks in water; accordingly it is possible to attain a degree of concentration in which the cylinder only just sinks, and thus exerts scarcely any pressure on the bearings.

The small apparatus which I used consisted of a longish glass vessel of rectangular section. The copper cylinder, which occupied almost the whole breadth of the trough, was 4.5 centim. in length and its diameter was 10 centim. The thickness of the sides was 1.8 millim. At the ends ebonite plates were cemented, and through them passed the axis, a glass rod 1 millim. in diameter, which projected a few millimetres on each side; the bear-

ings were small triangular ebonite plates which were fastened to the side of the glass vessel. The cylinder turned slowly and continuously with currents of 0.1 to 1 ampere. The motion gradually became slower, in the first place probably because the surface of the cylinder became rough, owing to electrolysis. After going for some time the motion appeared to become more uniform. Some experiments gave an approximate proportionality between the velocity of rotation and the strength of the current. It is possible that in the hands of a skilled technician this might lead to the construction of a continuous electricity meter for continuous currents.—Wiedemann's *Annalen*, No. 2, 1892.

#### ON A METHOD OF DETERMINING ELECTROMAGNETIC RADIATION.

BY PROF. KLEMENCIC.

The method applied by the author consists in bringing a thermo-element near a fine platinum wire heated by the electric vibrations, and measuring the increase of temperature of the junction. As a comparison the platinum wire is also heated by a constant current, and the rise of temperature of the junction is also measured. Two series of experiments were made. In one the author employed a form of secondary inductor which has frequently been used (two thin brass plates each 30 cm. in length by 5 cm. in breadth), and investigated the heating of a thin platinum wire 2 cm. in length. The observations showed a production of heat of 0.000155 calorie per second. In the second case, a single platinum wire 26.3 cm. in length was exposed to radiation, and the value 0.000088 calorie per second obtained. In both series of experiments Hertz's mirror was used with a distance of 1.44 metres between the focal lines. It may in addition be mentioned that a wave-length of 66 cm. corresponds to the primary inductors, that the Ruhmkorff was excited by three accumulators, and that the breaks were at the rate of 23 per second. Boys, Briscoe, and Watson (*Phil. Mag.* 1891, *xxi.* p. 44) determined the intensity of the electromagnetic radiation with the aid of the convection air-thermometer, and found the value 0.000685 calorie per second. The length of the wire they used was  $2 \times 103$  cm., and it was at a distance of 30 cm. from a couple of primary inductors of above 100 cm. in length. If the value found by the English physicists is referred to unit length of the irradiated wire, and if this is done also for the second value found by the author, the result is a production of heat in both cases of 0.000033 calorie per second. Owing to the great difference between the two methods, this agreement is of course only accidental.—*Wiener Berichte*, February 18, 1892.

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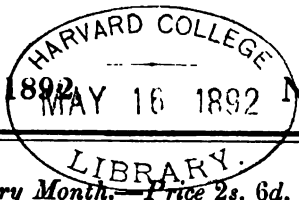
# CONTENTS OF N° 203.—*Fifth Series.*

XXXV. On the Absorption-Spectra of some Copper Salts in Aqueous Solution. By THOMAS EWAN, B.Sc., Ph.D., Dalton Scholar in Chemistry in the Owens College.....	page 317
XXXVI. On Chemical Equilibrium in Mixed Electrolytes. By Dr. G. GORE, F.R.S. ....	342
XXXVII. Note on the Resistance and Self-Induction of Branched Circuits. By Prof. A. ANDERSON, M.A. ....	352
XXXVIII. Remarks on Maxwell's Investigation respecting Boltzmann's Theorem. By Lord RAYLEIGH, Sec. R.S. ....	356
XXXIX. On an Experiment Illustrative of the Formation of Rocking Stones. By CHARLES TOMLINSON, F.R.S. ....	359
XL. Experiments upon Surface-Films. By Lord RAYLEIGH, Sec. R.S. ....	363
XLI. Wave Propagation of Magnetism. By JOHN TROWBRIDGE	374
XLII. Note on the Selective Absorption of Light by Optical Glass and Calc-spar. By EDWARD L. NICHOLS and BENJAMIN W. SNOW ....	379
XLIII. Notices respecting New Books:—F. KARRER's Guide through the Collection of Building-materials in the Imperial Natural-history Museum at Vienna; Mr. A. M. WORTHINGTON's Dynamics of Rotation .....	382, 393
XLIV. Proceedings of Learned Societies:—	
GEOLOGICAL SOCIETY:—Rev. J. F. BLAKE on the Rocks mapped as Cambrian in Caernarvonshire; Mr. W. SHONE on the Subterranean Denudation of the Glacial Drift, a probable cause of Submerged Peat and Forest-beds; Mr. A. C. NICHOLSON on High Level-Glacial Gravels, Gloppe, Cyn-y-bwch, near Oswestry; Mr. HORACE W. MONCKTON on the Gravels on the South of the Thames from Guildford to Newbury, and on the Bagshot Beds of Bagshot Heath; Messrs. A. J. JUKES-BROWNE and Prof. J. B. HARRISON on the Geology of Barbados .....	384-387
XLV. Intelligence and Miscellaneous Articles:—	
On the Intensity of the Radiation of Gas under the Influence of the Electrical Discharge: preliminary notice by K. Ångström .....	387
On the Repulsive Force of Radiating Bodies, by Peter Lebedew	391
An Electrolytic Experiment, by Leo Arons .....	395
On a Method of Determining Electromagnetic Radiation, by Prof. Klemencič .....	396



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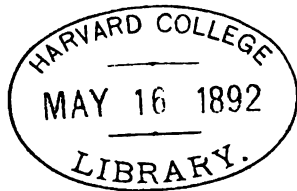
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[FIFTH SERIES.]

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MAY 1892.

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XLVI. *On the Resistances to Transverse Strain in Beams.*  
By ROBERT CRADOCK NICHOLS\*.

A COMMUNICATION was made to the Royal Society in 1855 by Mr. W. H. Barlow, in which a new theory was propounded to account for the amount of strength exhibited by bars or beams of cast iron subjected to transverse strain, which could not be reconciled according to any previously suggested hypothesis with the results obtained from experiments on direct tension.

Shortly stated, Mr. Barlow's theory was this: that in addition to the resistances to deflexion or rupture called into action by the compression of the fibres on the one side, and their extension on the other side of the bar, a further amount of resistance was developed by the lateral action of the fibres caused by the curvature of the bar, which he termed a *resistance to flexure*.

Mr. Barlow gave in his paper an account of a number of elaborate experiments which he regarded as establishing the truth of this theory, and further developed it in an algebraical form in a series of equations which were made to correspond with the experimental results.

The theory thus proposed has since been generally accepted and approved, and has continued to the present time to be regarded by the best practical authorities as the true explanation of the facts; though a doubt has been expressed

\* Communicated by the Author.

*Phil. Mag.* S. 5. Vol. 33. No. 204. May 1892. 2 E

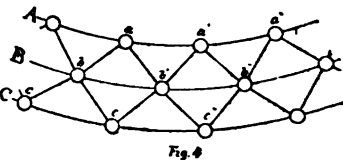
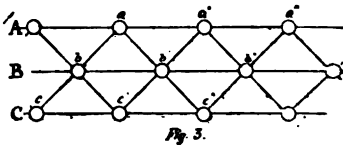
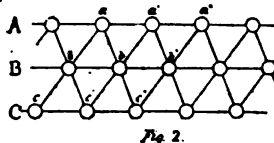
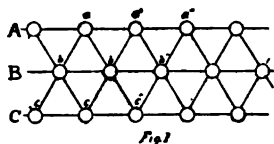
whether lateral action alone was sufficient to account for the whole of the extra strength which had been observed\*.

The use of cast iron as a material for beams and girders has been so much discredited, and to a great extent superseded by that of wrought iron and steel, that the practical importance of this question has greatly diminished since the date of Mr. Barlow's investigations. It may, however, be still regarded as one of some theoretical interest, and its true solution as not altogether devoid of practical value.

No explanation was given by Mr. Barlow of the manner in which his assumed *resistance to flexure* was supposed to act. It may be observed that, in addition to the ordinary direct resistances to extension or compression, another kind of resistance is known to come into operation when the particles of a body situated in one layer or set of fibres are laterally displaced relatively to those in a contiguous layer or set of fibres, as in the case of torsional or shearing strain.

The nature of this resistance may be illustrated by the accompanying diagrams. A, B, C (fig. 1) are supposed to represent three contiguous fibres or filaments,  $a a' a''$ ,  $b b' b''$ ,  $c c' c''$ , the particles of which they consist, in their original relative position. Then when these fibres are displaced, as in fig. 2, the distance between  $a$  and  $b$ ,  $b$  and  $c$  &c. is increased, while that between  $a$  and  $b'$ ,  $b$  and  $c'$ , &c. is diminished. Both these displacements will call into action resistances of a tensile or compressive nature, and constitute a shearing or a torsional strain according as the lateral motion is direct or rotatory.

In the case of direct tensile strain (fig. 3), where the displacement of all the particles is relatively similar, a like resistance must exist in consequence of the increased distance between the particles in contiguous filaments. But the resultant of these



\* Sir B. Baker, 'On the Strength of Beams, Columns, and Arches,' p. 10.

resistances being in the direction of the fibres, they are measured with, and undistinguishable from, the resistance to the elongation of the several filaments.

But if these form part of the extended portion of a bar subjected to transverse strain, and therefore undergoing flexure, as in fig. 4, the extension of the middle fibre being assumed to be the same as that of all the fibres in fig. 3, the distance between  $b$  and  $c$ ,  $b$  and  $c'$ , &c. will be increased to a greater extent than in the previous case of direct tension, and therefore an increased resistance developed between them. But, on the other hand, the distance between  $a$  and  $b$ ,  $a'$  and  $b$ , &c. will be less increased, and the resistances thereby caused will be less. So that unless the bending or flexure be extremely great, the aggregate resistances to the displacement of the particles of the middle fibre B will be the same, neither more nor less than that to its elongation to an equal amount by direct tension.

These considerations appear to present some *à priori* ground against the supposition of such a *resistance to flexure* as is assumed by Mr. Barlow, and they are further confirmed by the investigations of M. St. Venant\*, referred to and endorsed by Sir William Thomson in his article on Elasticity in the *Encyclopædia Britannica*.

M. St. Venant proved that, with the important practical exception of a thin flat spring, the resistances to the flexure of a rod or bar consist in "the mutual normal forces pulling the portions of the solid towards one another in the stretched part and pressing them from one another in the condensed part, and that the amount of this negative or positive normal pressure per unit of area must be equal to the Young's modulus ( $E$ ) at the place multiplied into the ratio of its distance from the neutral line of the cross section to the radius of curvature. . . . Hence the principal flexural rigidities are simply . . . . equal to the product of the Young's modulus into the principal moment of inertia of the cross section"†; that is to say, the moment of the resistances is the sum of the moments of the tensile and compressive stresses.

This had indeed been assumed, as Sir William Thomson remarks, without proof by earlier writers; but it was St. Venant who first gave the subject "satisfactory mathematical investigation," and "proved that the old supposition is substantially correct."

\* *Mémoires des Savants Etrangers*, 1855, "De la Torsion des Prismes, avec considérations sur leur Flexure."

† *Encyc. Brit.* vol. vii., art. "Elasticity."

Before proceeding to inquire further into the real cause of the actual amount of resistance found to exist in bars subjected to transverse strain, it will be desirable to examine somewhat closely some of the experiments detailed by Mr. Barlow, and the conclusions drawn from them by him for the purpose of establishing his theory.

His first set of experiments were made "in order to establish clearly the position of the neutral axis;" and he states that they "point it out as the centre of the beam in a manner so decided as to remove all further doubt on the subject, not only in the smaller strains but in the larger ones, which were carried to about three fourths of the breaking weight"\*..

Mr. Barlow's experiments were conducted with extreme care, and his measurements made with all the accuracy which circumstances would permit. He observes that "considering the very minute quantities which had to be measured, and the numerous causes of disturbance to which observations of such delicacy were liable, such as changes of temperature, or want of perfect uniformity in the dimensions or texture of the beams, the results exhibit much more regularity than could have been expected."

These experiments were made upon cast-iron beams or bars "7 feet long†, 6 inches deep, and 2 inches in thickness, on each of which were cast small vertical ribs at intervals of 12 inches: these ribs were  $\frac{1}{2}$  inch wide and projected  $\frac{1}{4}$  inch from the beam. In each rib nine small holes were drilled to the depth of the surface of the beam for the purpose of inserting the pins attached to a delicate measuring instrument, the intention being to ascertain the position of the neutral axis by measuring the distance of the holes in the vertical ribs when the beam was placed under different strains"‡.

Mr. Barlow does not state the distance between the holes, nor whether the accuracy of their relative distances was tested in any way. The only indication given on this point is the statement that the elongation at the lowest point measured was  $\frac{1}{12}$ ths of that of the outer fibres. This implies that the distance of the last hole from the lower (or upper) side was  $\frac{1}{4}$  inch, giving for the distance between the holes  $5\frac{1}{2}$  inches

\* Phil. Trans, 1855, p. 228.

† In the plate the beams are figured as 7 feet 4 inches long, and in another place in his paper Mr. Barlow refers to them as of this length, but in the absence of definite and consistent statement it may be concluded that the distance between the points of support was 7 feet, while 7 feet 4 inches was the total length.

‡ Phil. Trans. 1855, p. 225.

+8, or .6875 inch. It would, however, be impossible to regulate the distance with any very minute accuracy, and some considerable part of the irregularities observable in the measurements may probably be due to this cause.

"It will be observed," says Mr. Barlow, "that the extensions and compressions increase in an arithmetical ratio from the centre to the extreme upper and lower sides of the beam." If we substitute the word "neutral axis" for "centre," it is obvious that this must necessarily be the case; and any deviation from this law must be regarded as resulting from errors of measurement, inequality in the distances between the points measured, want of uniformity in the material, or other accidental causes.

It may therefore be assumed that if an arithmetical series be taken, approximating as nearly as possible to all the actual measurements, the quantities so obtained may be regarded as the corrected results of the experiments.

It is, moreover, to be noted that the extensions and compressions measured are those of a portion of the beam about 12 inches in length, extending therefore to a distance of about 6 inches from the centre on each side.

Each length was separately and minutely measured before being strained; but the variations in the original lengths, at least in the first series of experiments, do not exceed  $\frac{1}{500}$ th part of the whole, so that they will be inappreciable in their effect upon the amount of extension or compression as measured. The mean length was 12.25 inches.

But the maximum strain will exist only at the centre of the length of the beam, and that at any other part of it must be proportionate to its distance from the point of support. It follows that the strain at the centre of the beam will be

$\frac{42}{38.94} = 1.078$  times that indicated by the measurement of the extension or compression in the length of 12.25 inches, or nearly one twelfth greater\*.

The units of measurement in which the extensions and compressions are given by Mr. Barlow are  $\frac{1}{4390}$ th of an inch.

Taking, then, one series of experiments on the same beam subjected to successive loads we find these results:—

\* That is, so long as the limits of elasticity are not exceeded. If the beam should be overstrained at its lower side the strain at the centre may be considerably more in comparison with the mean strain for any distance on each side of the centre.

Cast-Iron Beam, 7 feet long, 2 inches wide, and 6 inches deep.

	With Load 2893 lb. at end = 5786 lb. at centre.			With Load 5133 lb. at end = 10,266 lb. at centre.			With Load 7373 lb. at end = 14,746 lb. at centre.			Load removed.		
	Measured Extension or Com- pression.	Corrected Extension or Com- pression.	Maximum Elongation or Contraction.	Measured Extension or Com- pression.	Corrected Extension or Com- pression.	Maximum Elongation or Contraction.	Measured Extension or Com- pression.	Corrected Extension or Com- pression.	Maximum Elongation or Contraction.	Measured Set.	Corrected Set.	Maximum Set.
Top of Section ..... }	.....	.....	- '000725	.....	.....	- '00127	.....	.....	- '00189	.....	.....	- '000302
Measure- } 1.	- 33	- 33.465		- 58	- 58.310		- 84	- 86.285		- 13	- 13.8	
2.	- 25	- 25.682		- 41	- 44.177		- 62	- 64.282		- 9	- 10.183	
3.	- 20	- 17.899		- 32	- 30.044		- 45	- 42.299		- 9	- 6.567	
4.	- 10	- 10.166		- 18	- 15.911		- 23	- 20.316		- 2	- 2.95	
5.	- 2	- 2.333		- 3	- 1.778		- 1	+ 1.667		- 1	+ .667	
6.	+ 5	+ 5.450		+ 11	+ 12.355		+ 23	+ 23.650		+ 3	+ 4.283	
7.	+ 15	+ 13.233		+ 29	+ 26.488		+ 48	+ 45.633		+ 11	+ 7.9	
8.	+ 21	+ 21.016		+ 42	+ 40.621		+ 71	+ 67.016		+ 11	+ 11.517	
9.	+ 28	+ 28.799		+ 54	+ 54.754		+ 88	+ 89.598		+ 15	+ 15.133	
Bottom of Section. }	.....	.....	+ '000633	.....	.....	+ '00120	.....	.....	+ '00196	.....	.....	+ '000390
			Neutral Axis above bottom of Section 2.795 inches.			Neutral Axis above bottom of Section 2.916 inches.			Neutral Axis above bottom of Section 3.055 inches.			Neutral Axis of set above bottom of Section 3.117 inches.



The deviation in the position of the neutral axis from the centre of the section under the smallest load, 5786 lb. at centre of beam, must be supposed to be due either to the points at which the extension and compression were measured not being accurately distanced vertically, or to some inequalities in the resisting power of different parts of the section. In any case these conditions will remain the same for the same beam under the different loads.

But it will be seen that there is a sensible and increasing displacement of the neutral axis with increasing loads in the direction of the compressed side of the beam, it being  $\cdot 121$  inch higher with 10,266 lb. than with 5786 lb., and  $\cdot 139$  inch higher with 14,746 lb. than with 10,266 lb., giving a total displacement of  $\cdot 26$  inch, or more than  $\frac{1}{4}$  inch.

A similar result is shown by an experiment with another similar beam loaded successively with 8000 and 16,000 lb. (see Table p. 404).

The displacement of the neutral axis between the loads of 8000 and 16,000 lb. is here  $\cdot 178$  inch.

Another series of measurements given by Mr. Barlow of the same beam inverted but with similar loading is valueless for the purpose of comparison, inasmuch as the measured lengths as loaded are compared with those taken before the inversion of the beam, and are therefore affected by its own weight in the opposite direction, and also affected by the considerable internal stresses caused by the overstrain to which the beam had already been subjected.

The amounts of displacement of the neutral axis may not appear considerable, but it must be remembered that within the limits of elasticity, and so long as the calculated stress at the lower side of the section does not exceed the direct tensile strength, all the facts are explicable upon the ordinary theory with the neutral axis in the centre; and it will be hereafter seen that for beams of rectangular section, even with extreme loads, no greater displacement is to be expected until the breaking weight is nearly reached, the utmost amount being about one tenth of the depth of the beam, or in this case about two thirds of an inch.

Another circumstance to be remarked in these experiments, and likewise in the other experiments made by Mr. Barlow hereafter to be referred to, but which does not appear to have been noticed by him, is that the elongations and contractions and the deflexions resulting from loading increase, not in the ratio of the load, but in a higher and increasing ratio.

Thus, for the 1st Beam, with a load of

5,786 lb.	the maximum elongation was	$\cdot 000633$	or	$\cdot 000109$	per 1000 lb.
10,266	"	"	$\cdot 00120$	"	$\cdot 000117$ " "
14,746	"	"	$\cdot 00196$	"	$\cdot 000133$ " "

Cast-Iron Beam, 7 feet long, 2 inches wide, and 6 inches deep.

	With Load 8000 lb. on Centre.			With Load 16,000 lb. on Centre.			Load removed.		
	Measured Extension or Compression.	Corrected Extension or Compression.	Maximum Elongation or Contraction.	Measured Extension or Compression.	Corrected Extension or Compression.	Maximum Elongation or Contraction.	Measured Set.	Corrected Set.	Maximum Set.
Top of Section ..... }	.....	.....	-000855	.....	.....	-00197	.....	.....	-0000588
Measure-ment. } 1.	-42	-38.445	Neutral Axis above bottom of Section 3.005 inches.				-3	-2.867	Neutral Axis of set above bottom of Section 5.022 inches.
2.	-27	-28.778					0	-0.733	
3.	-18	-19.111					+2	+1.4	
4.	-10	-9.445					-1	+3.533	
5.	+2	+0.222					+8	+5.667	
6.	+11	+9.889					+9	+7.8	
7.	+21	+19.555					+11	+9.933	
8.	+28	+29.222					+12	+12.067	
9.	+37	+38.889					+13	+14.2	
Bottom of Section. }	.....	.....	+000858	.....	.....	+00223	.....	.....	+000302

For the 2nd Beam, with a load of

8,000 lb.	the maximum elongation was	·000858	or	·000107	per 1000 lb.
16,000	„	„	„	·00223	„ ·000189 „ „

In the four experiments on solid rectangular beams 1 inch wide by 2 inches deep and 5 feet long, the mean initial deflexion was ·00035 inch per lb. of load, and the mean ultimate deflexion ·000524 inch per added lb., or half as much again, showing a diminished resistance as the curvature increased.

This fact is of the highest importance for the determination of the causes of the amount of transverse strength. If there were a *resistance to flexure* this should rather increase with the curvature. The consequence would be that the ratio of the elongation of the lower fibres, and of the deflexion, to the load should diminish as the curvature increases. It is found on the contrary to increase, and the fact of its doing so is fatal to Mr. Barlow's hypothesis.

Another material feature observable in these experiments, but not particularly noticed by Mr. Barlow, is that in all cases when the loads were removed the measured lengths did not return to their original dimensions but retained a permanent set. The amount of set shown is given in the last columns of the preceding tables, and will be hereafter again referred to.

Mr. Barlow assumes (1) that the resistance which he ascribes to flexure has the same effect as an addition to the tensile stress, and (2) that the amount of this addition varies with the degree of flexure, and also with the depth of the beam. But when he comes to determine the amount of this resistance in solid rectangular beams at the moment of rupture, he makes this addition, due to the resistance to flexure, a constant quantity, bearing a proportion to the tensile resistance of 1 to ·78! (Well may a doubt be expressed whether lateral action alone is sufficient to account for such an addition to the tensile resistance.) For a beam of different pattern he assumes that this constant is multiplied by the depth of metal and by the deflexion, and divided by the depth and deflexion of the solid beam.

In effect this is simply to treat the question as though the tensile strength were so much greater than it really is, the amount of the excess being taken at an arbitrary quantity, determined from the excess of transverse strength required to be accounted for, and modified to suit the case of beams of a different form in an equally arbitrary manner.

And no satisfactory account or explanation is given of this assumed enormous addition to the tensile resistance. It is clear that the relative lateral displacement of the fibres must

be, in comparison with their elongation or contraction, something extremely small, and the resistances thereby occasioned comparatively insignificant.

Mr. Barlow says "there are in fact two distinct changes of figure. There is the change produced by the tension and compression, which if acting alone would result in the figure *efgh* (a rectangle), and there is the change produced by the curvature, which if acting alone would result in the figure *lpnorm* (a similar rectangle with the upper and lower sides curved), the combination of these effects is necessary to produce the figure which a beam assumes under transverse strain"\*.

But this is to take into account twice over the greater part of the displacements by which the resistance is occasioned. If the area of the first figure represent the resistances caused by direct strain, it is clear that the addition caused by the second displacement cannot exceed that represented by the space not included in both areas.

What the experiments show us is a *loss* of resisting power with the increase of deflexion, manifested, as already pointed out, by an increasing ratio of deflexion to load, and therefore something absolutely the reverse of a resistance to flexure.

In addition to the conclusion already quoted as to the position of the neutral axis, which has been shown not to be confirmed by the experiments, Mr. Barlow makes this further comment upon them:—

"In the first beam a strain (load) of 5786 lb. caused an extension... at the outer fibres... = 30 divisions... therefore an extension of  $\frac{1}{1792.4}$  of the length. The beam was 7 ft. 4 in. long, 6 in. deep, and 2 in. thick, so that with a strain (stress) of  $\left(\frac{3 \times 88 \times 5786}{2 \times 12 \times 6} = \right)$  10,608 lb. at the outer fibres, the extension produced was  $\frac{1}{1792.4}$  of the length. But in referring to the experiments made by Mr. Hodgkinson, it will be seen that a force of 10,538 lb. applied by direct tensile strain extends cast iron  $\frac{1}{1056}$  of its length, being nearly double that exhibited by the beam."

Now an extension of this amount with such a stress, unless the limit of elasticity were exceeded, implies a modulus of elasticity  $E = 10538 \times 1056 = 11,127,028$  only; whereas the values of  $E$  deduced by Mr. Hodgkinson from his experiments on various samples of cast iron vary from 13,730,500 to 22,907,700, that for Carron CB being 17,270,000,

\* Phil. Trans. 1857, p. 471.

which is about the average. It must be remembered that the extension measured by Mr. Barlow is that of 12.25 inches of the length of the beam, and that the maximum extension at

the centre is therefore 1.078 times this amount or  $\frac{1}{1662.8}$ .

Taking the modulus of elasticity at 17,270,000 the extension due to a stress of 10,608 lb. applied by direct tension is

$\frac{10608}{17,270,000} = \frac{1}{1626}$ , or very nearly the same quantity. And

the extension above deduced from Mr. Barlow's measurements with this load of 5786 lb. is .000633, or  $\frac{1}{1580}$ , which is greater than that due to the direct tension if the modulus be as here supposed.

At all events Mr. Barlow's conclusion that the extension produced by direct tensile stress is nearly double of that caused by an equal calculated stress in the outer fibres in transverse strain, is not supported by the results of his own experiments. On the contrary, it appears that with moderate loads the extension is very nearly the same in both cases. But with extreme loads this is no longer true. The extension of the lower fibres will then be found considerably to exceed that which would be caused by a direct tensile stress equal to that calculated from the load on the supposition of the indefinite elasticity of the material, if such a stress could be applied without causing rupture.

It is, however, inconceivable that any such tensile stress exceeding that which is found by direct experiment to produce rupture can exist within the material. What, then, is the true explanation of the facts disclosed by the experiments?

In what Mr. Barlow terms "the existing theory of beams," as well as in the arguments upon which he bases his own theory, it is assumed that up to the point of rupture the elasticity of the material is unlimited; in other words, that the tensile or compressive stress always varies with the strain.

Now it is well known that this is not the case. It was found by Hodgkinson that with cast iron, although between a limit of about 5 tons tensile to 15 tons compressive stress the stress varied very nearly with the strain, when these stresses were exceeded the proportion of stress to strain diminished with increasing rapidity. Even within these limits the strict proportion which existed for either tensile or compressive strain of very small amount was not absolutely maintained, but with increasing stress the proportion of stress to strain gradually, though at first only very slightly, diminished.

And although experiments prove that rupture does not actually take place until the tensile strain is such as would correspond, if the elasticity continued unimpaired, to a tensile stress of at least 60 or 70 thousand pounds, the actual stress producing rupture, and which cannot therefore have been exceeded, is not more than a third of that amount. The experiments of Hodgkinson show a tensile strength for various samples of cast iron varying from 13,404 to 21,907 lb. Mr. Barlow's "experiments on tensile strain" give a stress of 15,747 to 22,035 lb. These experiments unfortunately do not show the amount of strain.

The annexed diagram (fig. 5) will then represent approximately the tensile strain and stress in units for strain of one

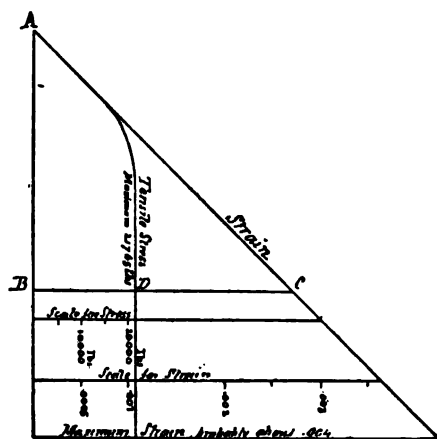


Fig. 5

inch for one thousandth part of elongation, and in units for stress of  $\frac{1}{20}$ th of an inch for every thousand pounds. This assumes the modulus of elasticity to be 20,000,000, which is about that indicated by the deflexions of a bar 5 feet long with moderate loads in the experiments of Mr. Barlow.

The excess of strain beyond its normal proportion to the stress may be termed the overstrain.

An unfailing indication that overstrain has taken place and that the stress has not maintained its proportion to the strain, is given when on the external forces causing the strain being removed the original condition is only partially restored and part of the strain remains as a permanent set. In the experiments of Mr. Barlow, already described, after the load of 14,746 lb. was removed, the distance between the lowest

points measured, which had been increased 88 units by the load, was reduced on its removal only 73 units. Similarly a load of 16,000 lb. caused an extension of 102 units, and its removal a contraction of only 89 units.

Now it is manifest that when a beam is transversely strained the amount of strain in any part of a given section will vary directly as the distance from the neutral axis. The stress, tensile or compressive, will, however, not necessarily vary in the same proportion, but will be that due to the strain, being nearly proportionate to it until the maximum stress—that which will ultimately cause rupture—is approached, but increasing no further than the breaking stress and maintaining practically the same amount until actual rupture commences.

And if the point A, in the last diagram, represent the position of the neutral axis of a beam undergoing transverse strain, and the distance below it AB on a vertical line represent the depth below it of any part of the section, if a horizontal line BC represent the tensile strain at that depth, then BD will likewise represent, on a scale  $\frac{1}{E}$  of that used in measuring

the strain, the tensile stress at the same depth.

It follows then that, when the limit of elasticity has not been exceeded, if the line CD (fig. 6), being the lower side of any section ABCD of a rectangular beam, subjected to transverse strain only\*, be taken to represent the stress per inch at that line, then the same line measured in units E times the length of those in which it measures the stress will represent the longitudinal elongation per unit of length of the filaments of the beam, or the strain at that line. Join AD BC: then G, the intersection of those lines, is the centre of gravity of the section, and also under the same condition the position of the neutral axis. And the length of any horizontal lines *ab* or *cd* between those lines will represent in similar units the stress per inch either compressive or tensile, as well as the contraction or elongation at such line.

Moreover, the areas of the triangles AGB, CGD, multiplied

\* That is to say, the sum of the longitudinal stresses at that section reckoned positive or negative according as they are tensile or compressive amounting to zero. Should the beam in addition to the transverse strain be subjected also to longitudinal strain, the conditions will be altered and the position of the neutral axis changed.

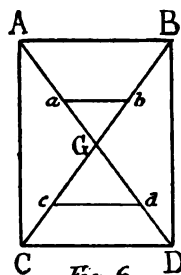
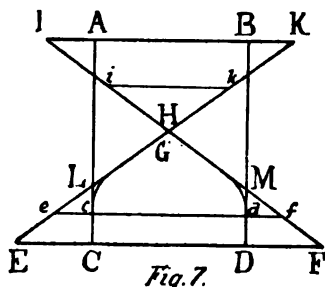


Fig. 6.

by the stress per inch at AB or CD will represent respectively the total compressive and tensile stresses on the section, and the sum of these multiplied by one third of the depth of the section will be the moment of horizontal stress at that section.

But if the limits of elasticity have been exceeded at CD, when CD is assumed to represent the stress per inch at that line, it will no longer represent the amount of elongation or the strain in units E times the length of those in which it



measures the stress, but the line representing the strain in such units will be longer than CD. Let this be represented by EF (fig. 7). Let H now be the position of the neutral axis. Draw EK, FI, straight lines through H, to meet AB produced in K and I. Then as before, any horizontal lines *ik* or *ef* drawn between these lines will represent the contraction or elongation at such lines. And if points *cd* be taken upon all such lines *ef*, equidistant from the vertical line through the centre of the section, so that the length of *cd* may represent the stress due to the elongation *ef*, and lines drawn through all such points from C and D to H, then the area of the figure enclosed by these lines and the base CD multiplied by the stress per inch at CD will be the total amount of tensile stress.

If the limit of elasticity has been also passed for compressive strain, the same operation must be repeated at all lines *ik*. But otherwise the area of the triangle IHK multiplied by the stress per inch at CD will be the total amount of compressive stress. And the sum of these areas each multiplied by the stress per inch at CD, and by the distance of their respective centres of gravity from H, will be the moment of horizontal stress about the neutral axis.

Inasmuch as the total amounts of tensile and compressive stress must be equal to each other, it is manifest that H and G will not under these circumstances coincide, but that as the strain increases after the limit of elasticity has been



In the case of cast iron it has been found, as already stated, that even with very moderate strains the ratio of stress to strain varies to some extent from its initial value  $E$ . But this variation does not become considerable for either tensile or compressive stress until it approaches that which ultimately produces rupture\*. And no very considerable error will result from assuming that the compressive stress varies directly with the strain in any bar of rectangular section subjected to transverse strain, and that the tensile stress also varies directly with the strain until it reaches the amount which ultimately produces rupture and then remains constant until the strain likewise reaches the point of rupture.

The diagram illustrates the geometric construction of a hyperbola. It features a central vertical axis with points I, A, B, K at the top and E, C, T, Q, V, D, F at the bottom. A horizontal line segment AB is drawn. Two intersecting lines, IK and EF, form an 'X' shape. A series of horizontal lines connect the arms of the 'X'. A curve, representing the hyperbola, is drawn through points L, M, N, O, P, Q, R, S, T, U, V, W, X, Y, Z. The construction involves the intersection of various lines and curves, with points labeled with letters and numbers to indicate specific locations and measurements.

Then if NP be taken to represent the maximum tensile stress, S, or a little less than the tensile breaking-stress, produce this line to R and S (equidistant from O), and assume RS to represent on a scale E times as great the elongation of the fibres at a depth below the neutral axis equal to half the depth of the beam.

\* It appears from the experiments of Mr. Hodgkinson that the breaking compressive stress of cast iron is generally from 100,000 to 130,000 lb. —Phil. Trans. (1857) p. 866.

directions. Then draw  $IK$  and  $EF$  parallel to  $RS$ , intersecting the vertical lines through  $N$  and  $P$  at  $A$  and  $B$ ,  $C$  and  $D$ , at a distance from each other equal to the depth of the beam, in such manner that the area of the triangle  $IHK$  may equal that of the pentagon  $CLHMD$ . Then  $ABCD$  will represent the section of the beam;  $H$  will be the position of the neutral axis, which will be slightly elevated above the centre of gravity,  $G$ , of the section;  $IK$  will represent the compressive strain or stress at the upper side of the beam; any horizontal lines  $ik$ ,  $lm$ , intersecting the lines of strain or stress  $IM$ ,  $KL$ , will represent the strain or stress at such line, any line  $ef$  intersecting the lines  $LE$ ,  $MF$ , will represent the strain, and the portion of it  $cd$  between  $LC$  and  $MD$  the stress, at such line, and  $EF$  and  $UD$  respectively the strain and stress at the lower side of the beam.

And the areas  $CLHMD$  and  $IHK$  will be the areas of maximum tensile stress and of an equal compressive stress respectively, and the sum of these areas each multiplied by the maximum tensile stress and by the distance of its centre of gravity from  $H$  will be the total moment of horizontal stress.

Let  $AB=b$ ,  $AC=d$ ,  $e$  = elongation per unit of length at a depth below the neutral axis equal to half the depth of the beam,  $HQ$ , the height of neutral axis above the lower side,  $=h$ ,  $MD=c$ , and  $h-c=g$ .

Then

$$\frac{NP}{RS} = \frac{S}{Ee}$$

Let this  $= \sigma$ ,  $g = h - c = \frac{HO \cdot NP}{RS} = \frac{d\sigma}{2}$ ,

$IK = \frac{b(d-h)}{g}$ , and the  $\Delta IHK$  = the pentagon  $CLHMD$ ,  
or  $\frac{b(d-h)^2}{g} = bg + 2bc = b(2h - g)$ .

Solving this equation with respect to  $h$ , we obtain

$$\begin{aligned} h &= d + g - \sqrt{2dg} \\ &= d \left( 1 + \frac{\sigma}{2} - \sqrt{\sigma} \right), \end{aligned}$$

which is the height of the neutral axis above the lower side of the section;

$$\therefore d - h = d \left( \sqrt{\sigma} - \frac{\sigma}{2} \right), \text{ and } c = h - g = d(1 - \sqrt{\sigma}).$$

And the moment of  $IHK$  about  $H$  is

$$\frac{1}{3} \frac{b(d-h)^3}{g} = \frac{bd^3}{6} \frac{(2\sqrt{\sigma} - \sigma)^3}{2\sigma};$$

the moment of LHM is

$$\frac{1}{3} b g^3 = \frac{b d^3}{6} \frac{\sigma^3}{2};$$

and the moment of LCDM is

$$\left(g + \frac{c}{2}\right) b c = \frac{b d^3}{2} (1 + \sigma - \sqrt{\sigma})(1 - \sqrt{\sigma});$$

Therefore the total moment of stress is

$$\begin{aligned} S \frac{b d^3}{6} \left( \frac{(2\sqrt{\sigma} - \sigma)^3}{2\sigma} + \frac{\sigma^2}{2} + 3(1 + \sigma - \sqrt{\sigma})(1 - \sqrt{\sigma}) \right) \\ = S \frac{b d^3}{6} (3 - 2\sqrt{\sigma}). \end{aligned} \quad (1)$$

Now if  $S_1$  be the maximum stress which would have existed in consequence of the loading at the lower side of the section if the elasticity had been perfect, the total moment of stress will be represented by  $S_1 \frac{b d^3}{6}$ ;

$$\therefore S(3 - 2\sqrt{\sigma}) = S_1.$$

Let  $\frac{S_1}{S} = r$ , then

$$\sigma = \left( \frac{3-r}{2} \right)^2.$$

And the strain at half the depth of section below the neutral axis is

$$e = \frac{S}{E\sigma} = \frac{S}{E} \left( \frac{2}{3-r} \right)^2; \quad (2)$$

the maximum tensile strain at C D represented by EF is

$$e_1 = \frac{2eh}{d} = \frac{2S}{E} \frac{1 + \frac{\sigma}{2} - \sqrt{\sigma}}{\sigma} = \frac{S}{E} \frac{4 + (r-1)^2}{(3-r)^2}; \quad (3)$$

the maximum compressive strain at AB is

$$e_2 = \frac{2e(d-h)}{d} = \frac{S}{E} \frac{2\sqrt{\sigma} - \sigma}{\sigma} = \frac{S}{E} \frac{1+r}{3-r}; \quad (4)$$

and the maximum compressive stress is

$$S \frac{1+r}{3-r}. \quad (5)$$

The amount of displacement of the neutral axis from the  
*Phil. Mag.* S. 5. Vol. 33. No. 204. May 1892. 2 F

centre of gravity is

$$h - \frac{d}{2} = d \left( \frac{1 + \sigma}{2} - \sqrt{\sigma} \right) = \frac{d}{2} \left( \frac{r-1}{2} \right)^2. \quad (6)$$

The foregoing equations are sufficient to determine the conditions under which the facts relating to transverse strength may be reconciled with those of tensile strength without recourse to the supposition of any kind of resistance other than the known resistances to extension and compression.

The truth of the theory and its adequacy to account for the facts shown by experiment may be tested by comparing the amounts of deflexion calculated to exist according to the theory with those experimentally determined.

For this purpose it is necessary to find the curve assumed by a beam, and its consequent deflexion, under the supposed condition of overstrain.

Now it is evident that the area CLHMD of maximum tensile stress is the same as that of an equal stress would be if the stress continued to vary with the strain down to the lower side of the section, and every horizontal dimension of the beam between LC and MD were reduced in the proportion which the actual stress at any horizontal line bears to that which would then exist at that line, that is as  $cd$  to  $ef$ .

Make  $tv = \frac{(cd)^2}{ef}$ , and draw lines from L and M through all such points  $t, v$ , to meet the base in T and V. Then the actual strength of the section ACDB is the same as would be that of the section ALTVMB if the stress continued to increase with the strain to its utmost limit. And its deflexion under any given load must likewise be the same.

The centre of gravity of the section ALTVMB is the point H, which has been already determined to be the neutral axis of the section ACDB as subjected to overstrain. And the neutral axis of ALTVMB will coincide with its centre of gravity.

The moment of inertia of this section about that point is readily found to be

$$\begin{aligned} I_1 &= \frac{bd^3}{12} \sigma \left( \frac{(2\sqrt{\sigma} - \sigma)^3}{2\sigma} + \frac{\sigma^3}{2} + 3(1 + \sigma - \sqrt{\sigma})(1 - \sqrt{\sigma}) \right) \\ &= \frac{bd^3}{12} \sigma (3 - 2\sqrt{\sigma}) = I \frac{r}{4} (3 - r)^2, \quad (7) \end{aligned}$$

(where  $I$  is the moment of inertia of the section ACDB about its centre of gravity), which is therefore the moment of inertia of the reduced section at the centre of the length of the beam.

The radius of curvature at the same point is determined by the equation

$$\frac{1}{R} = \frac{Wl}{4EI_1} = \frac{Wl}{EI_1 r(3-r)^2}, \dots \dots \dots (8)$$

where  $W$  is the central load, and  $l$  the length of the beam.

And the deflexion of the original beam, on the supposition of stress and strain varying together, would be

$$\delta_1 = \frac{Wl^3}{48EI};$$

$$\therefore \frac{1}{R} = \frac{48\delta_1}{r(3-r)^2 l^2}, \dots \dots \dots (9)$$

and the elongation of the fibres at a depth  $\frac{d}{2}$  below the neutral axis

$$e = \frac{24\delta_1 d}{r(3-r)^2 l^2}, \dots \dots \dots (10)$$

and the elongation at the lower side of the section

$$e_1 = \frac{6\delta_1 d}{l^2} \frac{4 + (r-1)^2}{r(3-r)^2}, \dots \dots \dots (11)$$

The amount of elongation varies directly with the deflexion being  $\frac{6\delta_1 d}{l^2}$  so long as the limit of elasticity is not exceeded.

But when this is the case, as indicated by an excess of actual deflexion over the normal amount, an increase of elongation will be occasioned in a larger ratio than the increase in the deflexion, owing to the excess of curvature being confined to the portion of the beam which is overstrained, that is to say, to the central part, and being greatest in the centre of the length. The distance from the centre of the beam to which this overstrain will extend will be as far as the point at which the maximum tensile stress  $S$  is the same as the calculated maximum tensile stress; that is to say, since the moment of stress varies as the distance from the point of support, at a distance  $\frac{S}{S_1} \frac{l}{2} = \frac{l}{2r}^*$ .

\* The overstrain actually continues to some extent to a greater distance, as the stress does not in fact maintain a strict proportion to the strain until it attains its maximum, as has been assumed for convenience of calculation. The exact solution of the problem would require  $S$  to be treated as a variable, which would introduce too great complexity. The error occasioned by the treatment of the question which has been adopted is not considerable, but causes the calculated deflexions, especially for the intermediate loads, to be somewhat less than the true amounts.

At any point in the beam between this and the centre, and at a distance  $x$  from the point of support, the maximum stress which would exist on the supposition of perfect elasticity will be reduced in the proportion of  $2x$  to  $l$ . In the equation for  $I_1$ , therefore, to obtain the moment of inertia of the reduced section at that point,  $\frac{2rx}{l}$  must be substituted for  $r$ , and

$$I_1 = \frac{Irx(3l-2rx)^2}{2l^3}; \dots \dots \dots (12)$$

and at this point, if  $x, y$  be the ordinates of the curve of deflexion, the origin being the point of support,

$$\frac{EI_1}{R} = EI_1 \frac{d^2y}{dx^2} = \frac{Wx}{2};$$

$$\therefore EI \frac{d^2y}{dx^2} = \frac{Wl^3}{r(3l-2rx)^2}.$$

Integrating between  $x$  and  $\frac{l}{2}$ , and noting that at the centre  $\frac{dy}{dx} = 0$ ,

$$EI \frac{dy}{dx} = \frac{Wl^3}{2r^2(3l-2rx)} - \frac{Wl^3}{2r^2(3-r)};$$

and when  $x = \frac{l}{2r}$ ,

$$EI \tan \alpha = -\frac{Wl^3(r-1)}{4r^2(3-r)}. \dots \dots \dots (13)$$

Integrating again between the same limits,  $y$  being equal to  $-\delta$  at the centre,

$$EI(y+\delta) = -\frac{Wl^3}{4r^3} \text{ h.l. } \frac{3l-2rx}{(3-r)l} - \frac{Wl^3x}{2r^2(3-r)} + \frac{Wl^3}{4r^2(3-r)}; \quad (14)$$

and when  $x = \frac{l}{2r}$ ,  $y = y_1$ ,

$$EI(y_1+\delta) = -\frac{Wl^3}{4r^3} \text{ h.l. } \frac{2}{3-r} + \frac{Wl^3(r-1)}{4r^2(3-r)}. \dots \dots \dots (15)$$

Again, at any point between  $x = \frac{l}{2r}$  and the point of support, the moment of inertia is unaffected by overstrain, and

$$EI \frac{d^2y}{dx^2} = \frac{Wx}{2}.$$

Integrating between  $x$  and  $\frac{l}{2r}$ ,

$$EI \left( \frac{dy}{dx} - \tan \alpha \right) = \frac{Wx^3}{4} - \frac{Wl^3}{16r^3};$$

therefore, adding (13),

$$EI \frac{dy}{dx} = \frac{Wx^3}{4} - \frac{Wl^3}{16r^3} - \frac{Wl^3(r-1)}{4r^3(3-r)}.$$

Integrating again between the same limits,

$$EI(y-y_1) = \frac{Wx^3}{12} - \frac{Wl^3}{96r^3} - \frac{Wl^3x}{16r^3} + \frac{Wl^3}{32r^3} - \frac{Wl^3(r-1)x}{4r^3(3-r)} + \frac{Wl^3(r-1)}{8r^3(3-r)};$$

therefore, adding (15),

$$EI(y+\delta) = \frac{Wx^3}{12} + \frac{Wl^3}{48r^3} - \frac{Wl^3x}{16r^3} - \frac{Wl^3(r-1)x}{4r^3(3-r)} + \frac{3Wl^3(r-1)}{8r^3(3-r)} - \frac{Wl^3}{4r^3} \text{ h.l. } \frac{2}{3-r}; \quad (16)$$

and when  $x=0, y=0$ ,

$$\therefore EI\delta = \frac{Wl^3}{48r^3} + \frac{3Wl^3(r-1)}{8r^3(3-r)} - \frac{Wl^3}{4r^3} \text{ h.l. } \frac{2}{3-r},$$

$$\delta = \frac{12Wl^3}{Ebd^3} \left( \frac{1}{48r^3} + \frac{3(r-1)}{8r^3(3-r)} - \frac{1}{4r^3} \text{ h.l. } \frac{2}{3-r} \right), \quad (17)$$

$$= \delta_1 \left( \frac{1}{r^3} + \frac{18(r-1)}{r^3(3-r)} - \frac{12}{r^3} \text{ h.l. } \frac{2}{3-r} \right); \quad (18)$$

where  $\delta_1$  is the normal deflexion on the supposition of perfect elasticity, and  $\delta$  the increased deflexion consequent upon overstrain.

Equations (14) and (16) are the equations to the curve for the portions of the beam between the centre and the distance  $\frac{l}{2r}$  from the point of support, and between that and the point of support respectively, the value of the constant  $\delta$  in both being determined by (17).

Before proceeding further, it will be well to recapitulate the leading features of the theory above developed, which may be termed the theory of *overstrain*.

In any beam or bar of rectangular section subjected to transverse strain, the form of the areas of equal resistance, shown in fig. 6, and the coincidence of the neutral axis with the centre of gravity, presuppose a condition of perfect elasticity; that is, that the resistance to the extension or com-

pression of the fibres varies directly with the amount of extension or compression.

When this condition does not continue to the point of rupture, but, as in the case of cast iron, the limit of elasticity has been passed for tensile, but not for compressive, strain before rupture takes place, the maximum tensile stress is that which will produce rupture by direct tensile strain. But this maximum stress will exist, after the limit of elasticity is passed, not only at the lower margin, but for some distance within the substance of the beam. The form of the areas of equal maximum stress will be that shown in fig. 7, and the position of the neutral axis will be raised above the centre of gravity of the section.

The same considerations will lead to the conclusion that when the limit of elasticity is passed before rupture for compressive, but not for tensile strain, the form of these areas will be that shown in fig. 9, and the position of the neutral axis will be depressed. When it is passed for both tensile and compressive strain, the form will be one of the two shown in fig. 10; and the position of the neutral axis will be raised or depressed according as the limit of elasticity is first passed for tensile or compressive strain, or as the maximum compressive or tensile stress is the greater.

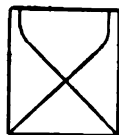


Fig. 9.

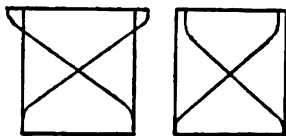


Fig 10

In each case the maximum tensile stress is supposed to be measured by the base of the section, and to be the unit of stress for both of the areas.

The same principles will apply to beams of any other section. In all cases the effect will be the same as if the dimensions of the section were reduced for some distance on each side of the centre of the beam, and the stress continued to increase proportionally to the strain without limit up to the point of rupture.

The results of four experiments made by Mr. Barlow on the deflexion of bars or girders of rectangular section under various loads increased by degrees to the breaking weight are recorded in his paper of 1855. In the following Tables the figures of the first and third columns are the loads and corresponding deflexions given by Mr. Barlow as the results of his first two experiments, the other quantities being calculated from them. The irregularity of the deflexions observed to be produced by the smaller loads renders it difficult to deter-



mine with certainty the modulus of elasticity of the metal employed ; but as in the first experiment four measurements, and in the second three, are given for loads not exceeding 712 lb., the average result of these may probably be taken as nearly correct ; and the modulus has been calculated from the mean deflexion for every pound of load up to 712 pounds, up to which amount it may fairly be assumed that stress and strain are directly proportionate, by the formula  $E = \frac{Wl^3}{4\delta b d^3}$ .

In the other two experiments no observations are recorded for loads between 40 and 712 lb., and those given for these loads do not appear sufficiently reliable to found any satisfactory conclusions upon them.

The moment of transverse stress in column 2 is  $\frac{Wl}{4}$ .

The normal deflexion in column 4 is that which would exist under each load if the limits of elasticity were not exceeded, and is calculated by the formula  $\delta_1 = \frac{Wl^3}{4Ebd^3}$ ; or if  $\delta_2$  be the deflexion already ascertained for any given load  $W_2$ ,  $\delta_1 = \frac{W}{W_2} \delta_2$ . The amounts so calculated vary little from the observed deflexions until the amount of tensile stress approaches that which would cause rupture by direct strain, after which the latter become considerably in excess.

The tensile stress per inch on the lower fibres is  $\frac{3Wl}{2bd^2}$  so long as the stress varies directly with the strain, but can never exceed the breaking stress. Mr. Barlow's experiments on the direct tensile strength of cast iron, made, as may be presumed, upon samples of iron similar in quality to those employed in his experiments on transverse strain, give 18,876 lb. as the mean breaking stress in eight trials. It must, however, be observed that these experiments give various values from 15,747 to 22,035 lb.; and that while the strength of a bar longitudinally strained is that of its weakest part, the tensile strength of the part of a bar transversely strained is precisely that at the centre of its length, and may generally be supposed to be more than the amount which, for the above reason, is obtained by experiments on direct longitudinal strain. If those experiments are rejected in which a distinct flaw was found to exist in the metal at the point of rupture, it will be found that the average stress actually supported without rupture in three of the experiments was 21,400 lb.; and it may fairly be assumed that the tensile strength at the

centre of the bars submitted to transverse strain may have been equal to the greatest tensile stress supported without rupture in any of the bars subjected to direct strain, which was 21,745 lb.

When the maximum tensile stress is first nearly approached the tensile stress at the lower fibres will be somewhat less than that given by the equation, but may be assumed to be determined by it until it is equal to a maximum somewhat below the breaking stress, and afterwards to remain constant at the same amount. If it had continued to vary with the load its amount would be that given in column 5, and the actual maximum tensile stress may be taken to be that in column 6.

Column 7 gives the ratio  $r$  of the two last values when the former exceeds the latter, and the quantities in the remaining columns are calculated by the equations above deduced from the theory of overstrain.

The annexed diagram (fig. 11) exhibits in a more striking form than the Table the relative proportion of the calculated deflexions to those measured and of both to the normal deflexion. The lengths of deflexion in the diagram are three times the actual amount.

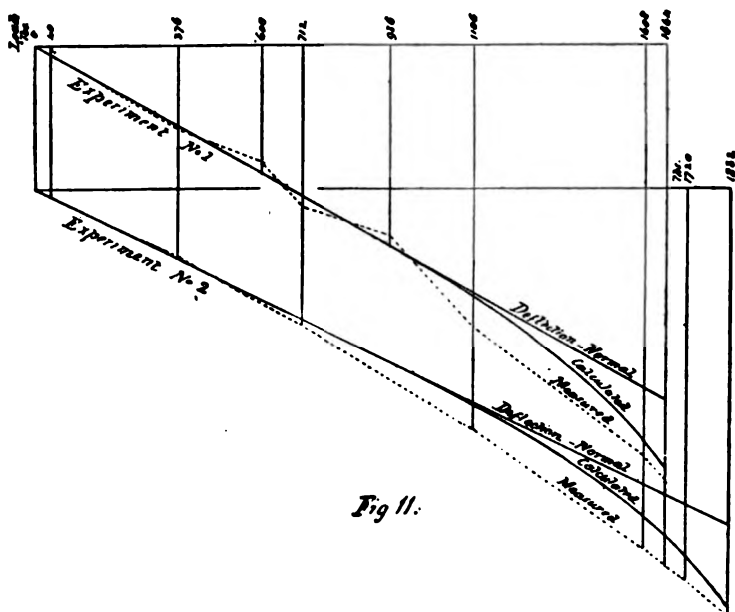


Fig 11.

It will be seen that in every instance except one, where there is obviously an error in the measured deflexion, the calculated amounts of deflexion are less than those observed. It

Experiment No. 1.—Bar 5 ft. 1 in. long (5 ft. between supports), width .975 in., depth 1.965 in.

Load or Weight applied.	Moment of Transverse Stress.	Measured Deflection.	Normal Deflection varying with the Load.	Tensile Stress on lower fibres if it varied with the Load.	Maximum Tensile Stress.	Ratio of two last.	Calculated height of Neutral Axis above C.G.	Maximum Compressive Stress.	Calculated Deflection.
W.		$\delta$ .	$\delta_1$ .	$S_1$ .	$S$ .	$\frac{S_1}{S} = r$ .	$h - \frac{d}{2}$ .		$\delta$ .
lb.	lb. in.	in.	in.	lb. per in.	lb. per in.		in.	lb. per in.	in.
40	600	.015	.01487	.956	.956				
376	5640	.145	.1398	8988	8988				
600	9000	.203	.2230	14340	14340				
712	10880	.280	.2647	17020	17020				
836	14040	.330 *	.3480	22375	21765	1.0280	.00019	22383	.3480
1160	17400	.490 *	.4312	27729	21765	1.2740	.01847	28676	.4376
1608	24120	.715	.5978	38438	21765	1.7660	.1441	48683	.6923
1664	24960	.765	.6186	39777	21765	1.8276	.1682	52491	.7372
.....	.....	broke.							

\* There is a manifest error in one or both of these. With an addition of only one fourth to the load the deflection measured is nearly one half greater.

$$E = \frac{1728 \times 216000}{4 \times .643 \times 7.398} = 19,535,000. \quad \text{Maximum elongation of lower fibres, .003777.}$$

Experiment No. 2.—Bar 5 ft. 1 in. long (5 ft. between supports), width .98 in. in depth, 2.02 in.

Load or Weight applied. W.	Moment of Transverse Stress. lb. in.	Measured Deflection. $\delta$ .	Normal Deflection varying with Load. $\delta_1$ .	Tensile Stress on lower fibres if it varied with the Load. $S_1$ .	Maximum Tensile Stress. lb. per in. 900	Ratio of two last. $\frac{S_1}{S} = r$ .	Calculated height of Neutral Axis above O G. $A - \frac{d}{2}$ .	Maximum Compressive Stress. lb. per in.	Calculated Deflection. $\delta$ .
lb. 40	600	.013	in. .0128	lb. per in. 900			in.		in.
376	5640	.115	.1203	8480	8460				
712	10680	.233	.2279	16020	16020				
1160	17400	.420	.3712	28100	21765	1.1963	.0010	26582	.3732
1608	24120	.625	.5146	36180	21765	1.6623	.1107	43317	.5697
1664	24960	.665	.5325	37440	21765	1.7202	.1310	46261	.6038
1720	26800	.680	.5505	38700	21765	1.7781	.1529	49484	.6412
1832	27480	.737	.5862	41220	21765	1.8939	.2017	56944	.7282
1888		broke.							

$$E = \frac{1128 \times 216000}{4 \times .361 \times 8.078} = 20,937,000. \quad \text{Maximum elongation of lower fibres, } .004078.$$

would appear from this that the maximum tensile stress might have been taken to be somewhat less. But it must be remembered that for convenience of calculation the stress has been assumed to vary with the strain until the former has reached its maximum amount, whereas in fact the overstrain commences considerably sooner. The result is that the calculated deflexion must be somewhat deficient, especially for the loads about one half the breaking weight. Making allowance for this circumstance, the calculations accord very fairly with the facts as observed.

Mr. Barlow relied much for the confirmation of his theory upon the fact that the excess of strength exhibited by solid beams does not appear to the same extent in flanged girders, or in beams of a form which he had made for the purpose of experiment in which an upper and lower flange were connected only at intervals, the effective section being therefore that shown in fig. 12, the space  $a c d b$  being vacant between the solid portions  $A a b B$  and  $c C D d$ . But this will evidently be the same on the theory of overstrain here proposed.

In such a beam before the point of rupture is reached, unless the intermediate space is a very small fraction of the total depth, the whole of the lower part of the section will be included in the area of maximum stress, and if  $d_1 = m d$  be the depth of the upper and lower solid portions, and the other terms and dimensions



Fig. 12.

as in the former case, then as before  $IK = \frac{b \bar{d} - h}{g}$ ,

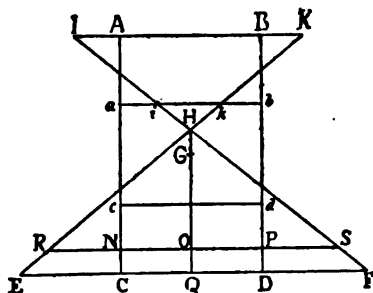


Fig. 13.

and (fig. 13)  $ik = b \frac{d - h - d_1}{g}$ ,

and the area of compressive stress  $I i k K$  being of necessity equal to the area of tensile stress  $c C D d$ ,

$$\frac{(d-h)^2}{g} - \frac{(d-h-d_1)^2}{g} = 2d_1$$

$$\therefore d-h = g + \frac{d_1}{2} = \frac{d}{2}(\sigma + m)$$

and

$$h = d\left(1 - \frac{\sigma + m}{2}\right), \dots \dots \dots (19)$$

the moment of tensile stress

$$Sbd_1\left(h - \frac{d_1}{2}\right) = Sbd^2\left(m - m^2 - \frac{m\sigma}{2}\right),$$

and the moment of compressive stress

$$S\frac{b}{3}\left(\frac{(d-h)^3}{g} - \frac{(d-h-d_1)^3}{g}\right) = S\frac{bd^2}{6}\left(3m\sigma + \frac{m^3}{\sigma}\right).$$

Therefore the total moment of stress is

$$S\frac{bd^2}{6}\left(6(m - m^2) + \frac{m^3}{\sigma}\right). \dots \dots \dots (20)$$

If we can find the value of  $\sigma$  the above equation will determine the breaking weight for a beam of this description, the moment of stress being  $\frac{Wl}{4}$ .

Now what appears to determine rupture is the maximum tensile strain. The amount of elongation with the maximum load supported was found in the examination of Mr. Barlow's first two experiments with solid beams to be respectively .003777 and .004078. For his third and fourth experiments the modulus of elasticity could not be satisfactorily determined, but assuming it to have been the mean of those found in the other two, or 20,236,000, the maximum elongation in these cases was .004185 and .004228. Remarking how nearly all these values approximate to each other, we may take the amount of elongation which will cause rupture at about .004.

In the case we are now considering the maximum elongation is

$$e_1 = \frac{2eh}{d} = \frac{S}{E} \frac{2 - \sigma - m}{\sigma}, \dots \dots \dots (21)$$

whence

$$\sigma = \frac{2 - m}{1 + \frac{Ee_1}{S}}. \dots \dots \dots (22)$$

With the value of  $\sigma$  so obtained the moment of stress will be

given by equation (20), and the breaking weight may thence be calculated.

Mr. Barlow made experiments on six patterns of beams of this description, four being tested of each pattern. In the Table on p. 426 are given the mean dimensions for each pattern, the breaking weights found by experiment, and those calculated as above.

Except in two instances (those of patterns 5 and 6, the second of which should on any theory be considerably stronger than the first, the breaking weights according to Mr. Barlow's formula being 4935 and 5533 lb. respectively) the agreement between the calculated breaking weights and those found by experiment is very remarkable; and it must be remembered that these values are not obtained from an empirical formula with arbitrary constants.

For a bar of square section diagonally strained the height of the neutral axis above the lowest point is determined by a cubic equation

$$h - \frac{d}{2} = \frac{2c^3}{3d^2}, \quad \dots \dots \dots (23)$$

where  $c = h - g$ .

But as  $\frac{c}{h} = 1 - \frac{S}{Ee_1}$ , the value of  $h$  may readily be found by approximation when  $e_1$  is given. Taking this as before at .004 for the maximum elongation at breaking point, and  $S$  and  $E$  as before, we find  $h = .5412d$ .

And calculating the moment of stress on the same principles as in the former examples, we obtain 2894 lb. for the breaking weight of a bar 2.835 inch in depth and 60 inches between the supports.

Four such bars were tested by Mr. Barlow, and the weights with which they broke varied from 2708 to 3268 lb.\*

The case of flanged girders would be of more importance if any reliance could be placed for practical purposes upon the element of strength in question. But as a test of the theory, the correspondence of the results deduced from it with the facts evinced by the three descriptions of beams already noticed is amply sufficient.

It may therefore be regarded as proved that the transverse strength exhibited by cast-iron bars or beams can be accounted for by tensile and compressive resistance without requiring either to exceed those found to exist by experiment on direct

\* Experiments on similar, but smaller bars, showed in proportion considerably greater strength, and the same result appears in comparing experiments with square bars squarely strained, and also with round bars. In fact it would seem as if the tensile strength of an iron casting must be greater near the surface than in the interior, as was found by Mr. Hodgkinson to be the case in regard to its compressive strength.

Beam 5 ft. 1 in. long (5 ft. between supports).

	Total depth. $d$ .	Depth between Ribs $d - 2d_1$ .	Width. $b$ .	$m = \frac{d_1}{d}$ .	$\sigma = \frac{S}{Es}$ .	Breaking Weight by Experiment.			Breaking Weight Calculated.
						Greatest.	Least.	Mean.	
Pattern No. 2.	in. 2.515	in. .54	in. 1.004	.3920	.3407	lb. 2748	lb. 2188	lb. 2468	lb. 2560
"	3.005	1.00	.995	.3936	.3531	3224	2972	3119	3127
"	3.997	2.03	1.00	.2473	.3714	4745	4204	4839	4474
"	4.04	1.08	.771	.3725	.3449	5405	4985	5141	4720
"	4.04	2.56	1.507	.1832	.3850	5405	4845	5147	5454
"	4.07	2.51	1.527	.1916	.3832	6525	5685	6000	5810



strain, and without the necessity for any other resistance to flexure.

And considering that if we regard an ideal vertical section through the centre of the beam, the whole of the resistances must be represented by the molecular forces between the particles on the opposite sides of that section, it is obvious that these are practically none but ordinary tensile and compressive stresses\*.

It is, however, only by considerable overstrain at the lower side of the beam that these forces can be enabled to supply the resistance which the facts prove to exist. And it is well known, as has already been observed, that an overstrain is always followed by more or less set after the pressures causing it are removed. And it is also well known that frequent alternations of strain and release cause such a modification of the internal structure, that with the lesser strains the variations between the proportions of stress and strain are reduced and the elasticity becomes more nearly perfect. And with the greater strains the probable effect will be of a similar nature.

The capacity of the material for overstrain will be reduced without any increase of the tensile strength; and if the extreme overstrains were frequently repeated, it is more than probable that the beam would be broken with a much less load than it supported without breaking on its first trial. Such an experiment may perhaps never have been made as to subject a beam repeatedly to anything near the breaking load. But the vibrations to which a beam is exposed when employed in a railway-bridge probably cause intermolecular strains of as great an amount with a similar change in the internal structure, and the failure of such beams with loads no greater than they have frequently borne before is unfortunately too common a circumstance.

The obvious conclusion is that the excess of strength for which Mr. Barlow, and it may be added the present writer, has been at such pains to account, and which, taking Mr. Barlow's theory for granted, practical engineers have treated as a real and important element of security, should not be regarded by them at all, but the efficient transverse strength of a beam should be computed from the tensile strength by the old method of calculation, and any extra strength exhibited in the trial of new castings disregarded as transitory and delusive.

\* There is probably also an infinitesimal resistance to flexure resulting from the lateral displacement of the particles. This must, however, be so extremely small as to be inappreciable in comparison with the resistances arising from tensile and compressive stress.

XLVII. *Flexure of long Pillars under their own Weight.*

By MAURICE F. FITZGERALD \*.

THE origin is taken at the upper end of the neutral axis, abscissæ being reckoned positive vertically downwards, and ordinates horizontal. The flexure is supposed small, and assumed to lie in a vertical plane. The symbols employed are as follows:—

$H$  = total height of pillar ;

$h$  = height below top of any point in it ;

$S$  = total shear on a section normal to neutral axis ;

$M$  = bending-moment ;

$w$  = weight of pillar per unit of length ;

$E$  and  $I$ , as usual, stand for the coefficient of flexural elasticity, and moment of inertia of cross section, respectively.

Taking a plane,  $AB$  (fig. 1), normal to the neutral axis, the shear on this plane is the component along it of the weight of the upper part of the pillar (whose top is supposed free); for small bending we have therefore

$$S = wh \frac{dy}{dh} \text{ nearly.}$$

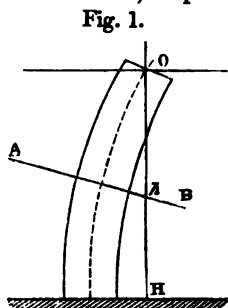


Fig. 1.

By well-known theorems,  $\frac{dM}{dh} = S$  and  $M = -EI \frac{d^2y}{dh^2}$ , which give by substitution,

$$EI \frac{d^3y}{dh^3} = -wh \frac{dy}{dh}.$$

By writing  $\frac{h}{H} = x$  and  $m = \frac{wH^3}{EI}$ , this takes the form

$$\frac{d^3y}{dx^3} = -mx \frac{dy}{dx},$$

in which, putting  $\frac{dy}{dx} = u$ , we get

$$\frac{d^2u}{dx^2} = -m x u,$$

a differential equation which enters into other questions.

The value of  $x (= \frac{h}{H})$  runs from 0 at top to 1 at foot of pillar;  $m$  has, except for pieces of fine wire a few feet in length, or for very unusually tall and large columns, only a small fractional value in practice.

\* Communicated by the Physical Society: read February 26, 1892.

Integrating the equation  $\frac{d^2 y}{dh^2} = -m \cdot \frac{dy}{dh}$  in series, we get

$$y = AU + BV,$$

where

$$U = x \left\{ 1 - \frac{mx^3}{2 \cdot 3 \cdot 4} + \frac{m^2 x^6}{2 \cdot 3 \cdot 5 \cdot 6 \cdot 7} - \frac{m^3 x^9}{2 \cdot 3 \cdot 5 \cdot 6 \cdot 8 \cdot 9 \cdot 10} + \dots \right.$$

V is another series, having  $x^3$  as a factor, and A and B are arbitrary constants.

Calling the first derived function, with respect to  $x$ , of U, U' and so on, the condition of a pillar free at top, and fixed initially vertically to a rigid base is expressed by

$$\frac{dy}{dx} = AU' + BV' = 0 \text{ when } x=1, \text{ i. e. at foot,}$$

and

$$\frac{d^2 y}{dx^2} = AU'' + BV'' = 0 \text{ when } x=0, \text{ i. e. at top,}$$

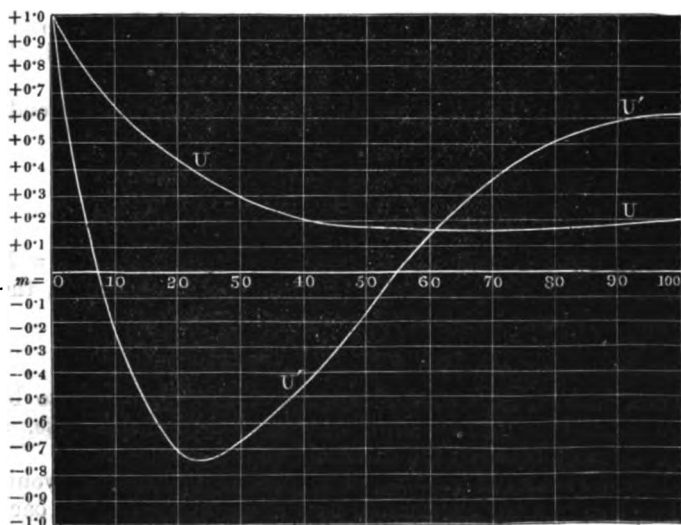
since there is no bending-moment at top.

As V contains  $x^3$  as a factor, the second of these gives  $B=0$ , and the first then requires  $U'=0$  when  $x=1$ . It will be found, on inspecting the curves plotted in fig. 2, that a value

Fig. 2.

$$y = U_{x=1} \quad \frac{d^2 y}{dx^2} = -mx \frac{dy}{dx},$$

$$u = U'_{x=1} \quad \frac{d^2 u}{dx^2} = -m u.$$



### 430 *Flexure of long Pillars under their own Weight.*

of  $m=7.85$  nearly is that required. For dimensions in feet, and for steel in which  $E$  = about 12,000 tons per square inch, this gives, on putting in the numerical values, and putting  $L$  = ratio of length to diameter,

$$H \text{ (in feet)} = \frac{8.1 \times 10^6}{L^2} \text{ for steel tubes,}$$

$H$  being here independent of the thickness, supposed small ; and

$$H = \frac{4 \times 10^6}{L^2} \text{ for round steel rods,}$$

as the limiting height of pillar which can stand without bending under its own weight. Thus for  $L=100$ , the maximum height is about 800 feet, giving a tube 8 feet diameter. For wires,  $L$  may be much greater ; for instance, the limit at which bending due to its own weight, of wire originally straight and vertical, size No. 28 B.W.G., must occur is about 1.8 feet.

All columns, in practice, naturally fall far within the limits here given. In connexion, however, with the inherent flexibility of very large masses under their own weight, even when direct crushing is prevented (say by external fluid pressure), it may be remarked that for  $L=4$ ,  $H=47$  miles, approximately ; so that a solid steel column 12 miles diameter would bend, even if prevented from bulging, if it were 50 miles high.

The only case of interest, besides that of a column fixed at its base and free at the top, above treated, seems to be that of a heavy upright column, held at top and bottom by external bending-moments so that the neutral axis is vertical at both ends, but otherwise free.

In this case, denoting by suffixes the values at each end, we have

$$AU_0' + BV_0' = 0, \quad AU_1' + BV_1' = 0,$$

$$AU_0'' + BV_0'' = M_1 H^2, \quad AU_1'' + BV_1'' = M_2 H^2.$$

$V_0'$  and  $U_0''$  are both zero identically ;  $U_0' = 1$ , and  $V_0'' = 2$ , which give  $A=0$  ;  $2B=M_1 H^2$  ; and, on substitution in the second and last of the above equations, we get

$$BV_1' = 0 \text{ and } M_1 V_1'' = 2M_2,$$

where, in  $V_1''$ , the value of  $m$  which makes  $V_1' = 0$  is to be inserted. The result shows that there is, in this case, a definite ratio between the external bending-moments.

Precisely similar results, as to producing bending, would take place in a bar accelerated by a force applied at its back

end, neglecting longitudinal sound-waves ; as also to a liquid filament retarded, if it possessed uniform stiffness in virtue of any internal motion.

Belfast, February 1, 1892.

Since the above was in print Prof. A. G. Greenhill, F.R.S., has sent to the writer a paper, published in the Proc. Camb. Phil. Soc. vol. iv. 1881, written by him for Prof. Asa Gray, on the greatest height of poles, masts, and trees, consistent with stability. The differential equation involved is, in Prof. Greenhill's paper, solved by the aid of Bessel's functions, and the investigation is extended to the cases of a solid cane, and a paraboloid of revolution, the general form of the solution for certain other solids of revolution being given. The results for a wire (allowing for a slight difference in the value assumed for  $E$ ) given by Prof. Greenhill are the same as those above. The function  $U'$  tabulated in the curve fig. 2 appears, from Prof. Greenhill's paper, to be connected with  $J_n(\kappa x^m)$  by the relation

$$U' = x^{\frac{1}{2}} J_{-\frac{1}{2}}(\kappa x^{\frac{1}{2}}).$$

Belfast, March 16, 1892.

**XLVIII. Note on the Change of Heat Conductivity on passing isothermally from Solid to Liquid. By C. BARUS.\***

**I**N an earlier paper† I gave an account of the volume expansion and of the change of thermal capacity of thymol, observed quite through the temperature interval  $\theta = 0^\circ \text{C.}$  to  $\theta = 50^\circ$  (melting-point), both for the solid and the liquid state. I have since considerably extended these observations. If  $\rho$  be density and  $c$  be specific heat, I found for liquid thymol ( $0^\circ$ – $50^\circ \text{C.}$ ),

$$1/\rho = 1.0113 / (1 - (.0007600 + 2\theta)\theta)$$

and  $c = .4475 (1 + .00238\theta)$ ; and for solid thymol ( $0^\circ$ – $50^\circ \text{C.}$ ),

$$1/\rho = .9631 / (1 - (.0002456 + 2\theta)\theta),$$

and  $c = .3114 (1 + .00302\theta)$ .

With these data in hand I was able to attack the corresponding problem in thermal conductivity. I made use of a somewhat modified form of H. F. Weber's‡ method, since it is well adapted for measuring small conductivities and meets other requirements of the present problem. If  $\Delta$  be the

\* Communicated by the Author.

† Cf. Proceedings American Acad. xxvi. p. 313 (1892).

‡ Wied. Ann. x. pp. 103, 304, 472 (1880).

thickness of the plate of thymol, and if  $k$  be its absolute heat conductivity ( $g/cs$ ), I found for the *solid* in two series of experiments relative to  $\Delta = .192$  centim.,  $k = 858/10^6$  at  $12^\circ$ ; in six series of experiments for  $\Delta = .153$  centim.,  $k = 866/10^6$  at  $12^\circ$ ; and finally, in eight series of experiments for  $\Delta = .107$  centim.,  $k = 354/10^6$  at  $11^\circ$ . Variation of  $\Delta$  was introduced as a check on the method. Hence the mean value of the absolute heat conductivity of solid thymol is at  $12^\circ$ ,  $k = 359/10^6$ , from which the corresponding datum for thermometric conductivity,  $\kappa$ , may be deduced by aid of the above results for thermal capacity and density. Thus  $\kappa = 1077/10^6$ .

In the case of *liquid* thymol at the same temperature, although I made a very large number of experiments, I only succeeded in obtaining six independent series faultlessly. These were made relative to  $\Delta = .107$  centim., and showed  $\kappa = 313/10^6$  at  $13^\circ$  and  $\kappa = 691/10^6$  at  $13^\circ$ , as mean values.

The data show that if the increase of thermal conductivity of thymol, observed on passing at  $13^\circ$  from liquid to solid be referred to solid thymol, the increment of absolute conductivity  $((k - k')/k)$  is 13 per cent., while the increment of thermometric conductivity is nearly 36 per cent. If the increments be referred to the conductivity of liquid thymol at  $13^\circ$ , they will necessarily be more striking, being 15 per cent. and 56 per cent. respectively.

Now in the analytical theory of heat, it is the thermometric conductivity which enters into the considerations of thermal flow, and the marked effect which changes from solid to liquid must necessarily produce is therefore obvious.

The comparison of the undercooled liquid with the solid may be deemed objectionable on the ground of possible polymerism. To say nothing, however, of the enormous complications of method introduced, little would be gained from an application of pressure. For in my work on the continuity of solid and liquid \* I showed that the passage from liquid to solid and back again, isothermally, by pressure, is perhaps always accompanied by hysteresis. Thymol is simply a convenient body in which the volume lag is pronounced, and is observable at ordinary temperatures and pressures, whereas in other substances the same phenomenon is exhibited at higher temperatures and pressures. Indeed it seems idle to ascribe to the molten liquid a more intimate relation to the solid than the undercooled liquid, unless it be clearly specified which this relation is.

\* American Journal, xlii. p. 125, 1891; cf. p. 140.

XLIX. *Choking Coils.*By Professor JOHN PERRY, *D.Sc., F.R.S.\**

**T**HERE is eddy-current loss of power in all the conducting masses of a choking coil. Hence a choking coil is really a transformer with one primary coil and many secondaries, and much magnetic leakage. In a transformer with many coils, whether or not they have magnetic leakage, it may be shown that any given group of secondaries of given numbers of turns and resistances may be replaced by one secondary without affecting the currents in the other coils; and we may take a choking coil to be a transformer with a primary coil of  $N$  turns and resistance  $R$  ohms, with  $C$  amperes flowing at any instant, the potential difference at its terminals being  $V$ , and a secondary coil closed on itself of  $n$  turns, resistance  $r$  ohms, and current  $c$  amperes.

If we assume that the induction per square centimetre  $\beta$  is the same everywhere, and if it follows the law

$$\beta \text{ in C.G.S. units} = \sum a_i \sin(ikt + e_i),$$

the average power in watts, wasted in eddy currents in the iron per cubic centimetre is

$$6.25 \times 10^{-13} r^2 k^2 \sum i^2 a_i^2,$$

if the specific resistance of the iron is taken to be  $10^4$  C.G.S. units. It is less at higher temperatures, being inversely proportional to the specific electric resistance of the iron. The iron is supposed to be of wire of radius  $r$  centimetres. Even when we leave the eddy-current loss in the copper out of account, it is to be remembered that the induction is not uniform in the section of a wire, nor is the average induction in each wire the same for all the wires, and therefore the real loss of power in the iron by eddy currents is always greater than the result of applying this formula.

I am going to assume that one secondary coil with no magnetic leakage may be substituted for all the eddy-current circuits, and this is the same as assuming the truth of the above rule. I ignore magnetic leakage because this is only a preliminary note, and such experiments as have hitherto been made do not enable me to take account of it, for there are no experimental measurements as yet of the want of uniformity of the induction.

The equations of the two circuits are

$$V = RC + N\theta I \quad \text{and} \quad 0 = rc + n\theta I,$$

\* Communicated by the Physical Society: read March 11, 1892.

if  $I$  is the total induction ( $10^8$  C.G.S. units being taken as the unit of induction). If

$$A = NC + nc \quad \text{and} \quad q = N^2/R^2 + n^2/r^2$$

(the term  $n^2/r^2$  being really negligible), the fundamental equation for calculating  $I$  is

$$A + q\theta I = NV/R. \quad \dots \dots (1)$$

Given the law connecting  $A$  and  $I$  and the resistances and  $V$ ,  $I$  may be calculated, and consequently  $C$  and  $c$ . Now in ordinary practical transformer calculations  $A$  may be neglected in the equation, even with the most complex law of magnetization; and it is this that causes calculations of the induction and secondary currents and voltages in the most complex cases, and even the primary current, unless when there is a small load on the transformer, to be exceedingly easy even when the coils are curiously connected with condensers and choking coils, and when there is much magnetic leakage. But in our present case, it is  $A$  itself which is wanted, and another method of working must be adopted. In fact, the value of  $C$  does depend very much upon the law of magnetization.

However complicated the magnetic law may be, it can be expressed in the shape :—

If 
$$I = \sum A_i \sigma_i \sin ix,$$
 then

$$A = \sum A_i \{ \sin (ix + f_i) - b_i \sin 3ix + m_i \sin 5ix - \&c \},$$

$x$  being any quantity which increases continually. To be strictly accurate, even as well as odd harmonics of  $ix$  exist in  $A$ , and one of my students, Mr. Fowler, has worked them out for some of Prof. Ewing's curves; but the above formula has been found by Mr. Field to be sufficiently accurate. Of course, instead of  $ix$  we may have  $(ix + e_i)$  in the above general expression.

When there is no hysteresis,  $f_i = 0$ . When there is constant permeability (no hysteresis and no saturation), not only is  $f_i = 0$ , but  $b_i = 0$ ,  $m_i = 0$  &c., and  $\sigma_i = \sigma_1$ .

If  $\mu$  the magnetic permeability of the iron is constant and the magnetic circuit is altogether of iron, as it always ought to be both in transformers and in choking coils,  $\sigma_i$  stands for  $4\pi a \mu 10^{-9}/\lambda$ , where  $a$  is the area of cross section of the iron in square centimetres, and  $\lambda$  is the average length of the induction solenoids in centimetres,

Equation (1) becomes in the most general case

$$NV/R = \sum A_i \{ \cos f_i \sin (ikt + e_i) + (\sin f_i + qik\sigma_i) \cos (ikt + e_i) - b_i \sin 3(ikt + e_i) + m_i \sin 5(ikt + e_i) \};$$



and hence, if  $V$  or  $I$  is given as a periodic function of the time, the other can be found and  $A$  and therefore  $c$  or  $U$ .

If  $V$  is a simple sine function of the time,  $I$  is so also, with very great, but not perfect accuracy. Assuming that  $I$  is a simple sine function, the neglected terms in  $V$  can now be calculated. The only problem, however, of importance is the calculation of  $C$  assuming that  $V$  follows the law  $V = V_0 \sin kt$ .

We may take  $q = N^2/R$ . Hence

$$-I = (V_0/Nk) \cos kt$$

very nearly, and if  $e = n^2 \sigma k/r$ , being called the eddy-current effect,  $f$  being the hysteresis term,

$$C = V_0 \left[ (1 + 2e \sin f + e^2)^{\frac{1}{2}} \sin \left\{ kt - 90^\circ + \tan^{-1} \left( \tan f + \frac{e}{\cos f} \right) \right\} - b \cos 3kt - m \cos 5kt \right] \div N^2 \sigma k \quad (2)$$

We see that the effect of eddy currents without hysteresis is to increase the amplitude of the important term in  $C$ , and to produce a lead of  $90^\circ - \cot^{-1} e$ , whereas the effect of hysteresis without eddy currents is to keep the amplitude unaltered and to produce a lead  $f$ . If  $f$  is put equal to 0, that is if we assume no hysteresis, we obtain results which seem to be in accordance with such experimental observations as have yet been made.

The effective current  $\bar{C}$  (if  $\bar{V}$  is the effective voltage), with constant permeability, is  $\bar{C} = \bar{V}/N^2 \sigma k$ . With hysteresis (or with no hysteresis but some saturation of the iron), but no eddy currents,  $\bar{C} = 1.02 \bar{V}/N^2 \sigma k$ , taking  $b$  as .2.

With eddy currents and hysteresis,

$$\bar{C} = \bar{V} \sqrt{1.04 + 2e \sin f + e^2} / N^2 \sigma k.$$

The average power given to the choking coil or average value of  $\bar{V} \bar{C}$  is

$$\bar{V} \bar{C} (e + \sin f) / (1 + e^2 + 2e \sin f),$$

neglecting the small terms due to  $b$  and  $m$ , and this may be done in all cases where there is not much saturation.

Probably there are always traces of the terms in  $3kt$  and the higher harmonics in both  $V$  and  $I$ , but they must certainly exist in either  $V$  or  $I$  even when there is not much saturation.

It almost seems that in a choking coil we have found what has long been looked for, a method of increasing frequency by mere magnetic means. A condenser shunting a non-inductive part of the circuit would receive currents

in which the higher harmonics would be greatly magnified in importance.

To show the magnitude of the terms in (2) I will take a well-known 1500-watt transformer, unloaded, as a choking coil. Here  $q=7837$ . The total average power wasted in heating the iron being 40 watts, I assume that this is altogether due to eddy currents. Power wasted in eddy currents being  $\pi^2 V_0^2 / 2rN^2$ , we have  $\pi^2/r=2.117$ , when  $V_0=2828$ . An eddy-current coil which would replace all the eddy-current circuits is a coil of 2 turns whose resistance is about 1.9 ohms, short-circuited on itself.

$$e=0.38, \text{ if } k=600.$$

It is obvious that  $e$  is proportional to  $k$  and to the square of the radius of the iron wire.

Assuming constant permeability and no eddy currents,

$$C=0.074 \sin (kt-90^\circ).$$

With some saturation but no hysteresis,

$$C=0.079 \sin (kt-69^\circ.2)-0.148 \cos 3kt-0.037 \cos 5kt,$$

if  $b=0.2$ ,  $m=0.5$ .

These values of  $b$  and  $m$  are usually employed by me for such magnetizations as are common in transformers. When I assume the existence of hysteresis, I take  $f$  about 20 degrees.

*L. The Recognition of Changes of Curvature by Means of a Flexible Lath.* By SPENCER UMFREVILLE PICKERING, F.R.S.\*

**I**F when a number of experiments are plotted out they form a figure exhibiting any sudden changes of curvature, it will very rarely happen that the position of these changes can be located, or even that their existence can be recognized, by mere inspection. To search for them by deducing various equations mathematically, involves an expenditure of time which is quite prohibitory, at any rate in the case of a figure with many breaks in it; and it is therefore highly desirable that some more expeditious method, such as the graphic method which I have adopted in my work on Sulphuric Acid (Chem. Soc. Trans. 1890, pp. 64, 331), should be shown to be reliable. I trust that the following examination of various cases will show:—(1) that this method leads to the same conclusions as does the mathematical method, which, as Mr. Lupton says, has been found to express physical facts “in the great majority of cases in Physics and Chemistry”—that of fitting on parabolas of the form

$$y=a+bx+\dots zx^n;$$

\* Communicated by the Author.

(2) that the evidence as to the existence and position of the breaks obtained by this method is certainly not dependent on the taste of the draughtsman ; and (3) that the splitting-up of the figure into different sections is due to the special nature of the figure, and not to the fact that any figure, whatever may be its nature, will split up into sections of any defined character provided the sections taken are sufficiently small.

Mr. Hayes has recently shown (*Phil. Mag.* vol. xxxii. p. 99) that the mathematical basis of the graphic method is sound ; that continuity is the essential feature of a curve formed by a lath when bent by forces applied near its extremities ; and that the curve is of a high degree of generality, and superior in this respect to the parabolic equations ordinarily employed. The practical results, moreover, which have so far been obtained by the method argue strongly in favour of its validity : various properties of the same solutions, though forming figures of totally different general appearance, all indicate consistently changes at the same strengths ; these strengths correspond, moreover, to solutions of definite composition ; and one of the hydrates thus indicated has been subsequently isolated in the solid condition.

#### *Experimental and Graphic Errors.*

The known magnitude of the experimental error is the chief criterion by which the legitimacy of any particular representation of a series of points can be determined ; and no representation should be accepted if it attributes to those points an apparent error, either greatly in excess of, or greatly inferior to, the known experimental error. If, moreover, as occasionally happens, two different drawings show the same value for the apparent errors of the points which they are supposed to represent, we are bound to accept the simplest of the two, unless any independent evidence in favour of the other be forthcoming.

The experimental error may generally be determined satisfactorily by a repetition of the individual determinations. In the present case various series of freezing-point determinations were taken as instances for investigation ; each series was performed in duplicate, fresh solutions being made for the duplicates, and if any exceptionally large difference appeared in the results, further repetitions were made. The solutions used in the repetitions were all of the same strength\*, and the arithmetical mean of the various observations gave the mean result at this strength ; each of these mean results gives

\* Slight errors in composition doubtless exist, but the total error may, for convenience sake, be regarded as being entirely due to the readings of the thermometer.

one "point" for diagrammatic purposes. The mean error of each of these points was determined in the usual way by the equation

$$\sqrt{\frac{\alpha^2 + \beta^2 + \dots}{n(n-1)}},$$

in which  $\alpha$ ,  $\beta$ , &c. are the differences between the individual observations and the arithmetical mean of them, and  $n$  the number of those observations.

To determine the relative acceptability of any drawing as a representation of series of experiments, several considerations must be taken into account:—

(1) The actual magnitude of the average apparent error of the points as compared with the drawing.

(2) The number of points represented by it as showing an exceptionally large and improbable error.

(3) The grouping together of errors with like signs.

(4) The equivalence of the sum of the *minus* errors to that of the *plus* errors.

As far as I know, no method has been proposed for taking proper account of any of these points except the first, still less for combining them so as to get a single value to represent the general acceptability of the drawing; and although the method which I have adopted in the following pages might be improved in abler mathematical hands, I think that it will be found to approximate closely to a mathematically correct method, and it is at any rate convenient, and seems to lead to results which are fair from all points of view. I may mention that it was not till after I had adopted this method under the impression that, though fair, it was entirely arbitrary, that I found that it could be justified mathematically.

1. *The Average Error.*—There is no difficulty about this; I represent it by  $e_1$ . It is generally the form of error which is alone considered; but I think that it is of less importance than the others, for it is possible to make a palpably unjustifiable drawing which yet attributes no more than the average experimental error to the points.

2. Judging from experimental results, the number of points which may reasonably be expected to show an error greater than twice the average experimental error is, in a case where each point is the mean of several determinations, between 1 and 2 in every ten, or a proportionately smaller number showing greater errors. On this principle the excessive errors may be estimated by

$$e_2 = \frac{s - m2e}{.1ne},$$

in which  $s$  is the arithmetical sum of those errors which exceed

twice the average experimental error  $e$ ,  $m$  the number of points exhibiting this excessive error, and  $n$  the total number of points in the drawing. If  $e_2$  is less than unity, unity should be substituted for it.

Referring to this error, Mr. Hayes has recently written to me as follows:—"I have been looking into the values for your  $e_2$  error, and find reason to think them perfectly fair, or, if they are unfair at all, it is in giving too modest an estimate of this error. The ideal values of  $e_2$ , I find to be about  $\frac{1}{2}$ , and any value for it greater than, say, 2 would be highly improbable. With a limited number of points, the fact that  $e_2$  was less than  $\frac{1}{2}$  (or 1) would prove nothing. I am inclined to think something involving the ratio of the found sum,  $s$ , to the theoretical sum,  $s'$ , would be more definite. Your numbers are hardly large enough for big values of  $s$ , since they vary approximately as  $s$  only. I should suggest  $\left(\frac{s}{s'}\right)^2$  as a suitable expression for  $e_2$ , calling it only 1 if it were less than, say, about 3 or 4."

3. The probability of a drawing will generally vary in some inverse ratio with the number of errors with like signs which it represents as occurring consecutively. A group of 6 errors with similar signs is evidently less probable than two separate groups in different parts of the drawing with three each, so that we cannot get any estimate of the relative probability of different drawings by comparing the sum of the numbers of errors with like signs occurring in groups; nor will, I think, the sum of the squares of these numbers lead to a just estimate, for it appears to me that a group of 6 like errors is more than twice as improbable as two groups of 3 each. I have therefore taken the sum of the cubes, and as the actual number thus obtained will be dependent on the total number of experiments dealt with, I have divided this sum by 5 times the number of experiments—

$$e_3 = \frac{m_1^3 + m_2^3 + \dots}{5n}.$$

In determining  $m_1, m_2$ , &c. the intervention of a *nil* error is counted as a change of sign; and, as in the previous case, the value of  $e_3$  is never allowed to fall below unity. It will = 1 if, say, in twenty points we get ten groups of 2 similar signs, four groups of 3, or one group of 4 with one group of 3 and one group of 2.

I was led to select 5 as the coefficient of  $n$  by determining what coefficient was required to make  $e_3=1$  in the case of numerous series of imaginary errors constructed by drawing lots for the signs and casting dice for the magnitude. For such a purpose the faces of the dice must be marked so as to corre-

spond with the values given by a probability-curve, namely, 2, 6·7, 12, 17·1, 23·3, and 38·9, average 16·7; and it must be remembered that all numbers below a certain value, depending on the scale used, will count as 0 in the practical examination of results. It was found in this way that the average value of the coefficient of  $n$ , when the total number of points examined was 9 to 18, was a little over 4, so that the 5 which I have taken leaves some margin beyond the average value. The nature of the  $e_2$  error is obviously such that it may lead to wrong conclusions in some cases: judging from the results with dice, I should say that with the coefficient 5 we might expect  $e_2$  to be rather greater than unity in 14 cases out of 50, but that in only 2 cases out of 50 would it reach the value 2.

4. The equivalence or otherwise of the sum of the opposite errors need not, I think, be taken into consideration. With the mathematical method here adopted we ought to get an exact equivalence; and if in using the graphic method we make a drawing in which there is a great want of equality, that drawing must be rejected, and a better one made. At the same time I do not think that strict equality should be sought, for, unless the number of points available is very large (some hundreds), the equal balancing of the majority of the errors of different signs may be upset by an accidentally large error in one or two of them. In this respect I think that the graphic method is superior to the mathematical one; for making the sum of the errors of opposite signs equal may be a distinct source of inaccuracy. Thus, if eighteen out of twenty points lie evenly about a straight line, we ought generally to accept a straight line as a representation of them; the mathematical method would, however, lead to the adoption of a curve in nearly every case of this description. Similarly, a curve deduced mathematically from a given number of experimental points will, when produced, nearly always deviate much farther from the points beyond those utilised, than will a curve drawn with the lath.

The total error,  $E$ , of a drawing or formula is taken to be the product of  $e_1$ ,  $e_2$ , and  $e_3$ ; and in any good representation this product will differ very little from  $e_1$ , and, consequently, very little from the ascertained experimental error.

Opinions will no doubt differ as to the relative importance of the three errors; but whatever be the demerits of the method adopted, it will, I think, be found to be fair, and it will also be found that we shall generally arrive at the same qualitative, if not quantitative\*, estimate of the relative merits

\* The  $e_1$ ,  $e_2$ , and  $e_3$  errors will naturally have different relative values according to the different peculiarities of the figures under investigation.

of various drawings, whether we consider any one of the three errors separately, or the combined results of all of them. By taking account of the extent to which  $e_1$  is less than the experimental error, and of the extent to which  $e_2$  and  $e_3$  are less than unity, it would obviously be possible to estimate the improbability of a drawing which follows the experiments too closely, as well as that of one which does not follow them closely enough, such as is here alone considered.

### *Examination of Case I.*

The first series of results examined consisted of the freezing-points of solutions of propyl alcohol in water from 0 to 32 per cent. in strength. They are given in the first part of Table I.\* The average experimental error is  $\cdot 0215^\circ$ . The figure which I consider they form is represented by A B, fig. 1 (p. 445). Such a drawing represents an average apparent error of  $\cdot 0275^\circ$  in the experimental points (column III. Table II.), and, as the  $e_2$  and  $e_3$  errors are less than unity, the total error of the drawing is  $\cdot 0275$  also, or 1.28 times the ascertained experimental error, an agreement as close as could be expected when dealing with a comparatively small number of points †. When drawn as four curves of equal length, we get a change of curvature at the same place as in the two-curve drawing; and, consequently, a slight diminution in the total error—to 1.07 times the experimental error (column v.),—but so slight that it would afford us no justification for accepting such a drawing in preference to the much simpler two-curve one, this latter being also in harmony with the experimental error ‡.

\* It was subsequently ascertained that the propyl alcohol here used was not quite pure, but this will not affect the results for the present purposes. Series of determinations have been made with a purer specimen, and the nature of the figures and the position of the breaks were found to be the same, though the magnitude of the depression was slightly different.

† Any drawing must, in the case of the present results, pass through the zero point, the freezing-point of pure water, for all the other points are determined by comparison with this. Also, any two consecutive curves must always be drawn so as to meet, since the property must be a continuous function of the strength. It has not been thought necessary to give the readings of the curves here, or the values given by the equations in Table III., but only the differences between them and the experimental points.

‡ Since writing the above I have done a good deal more work on the subject, and consider that a closer agreement between the apparent error of a drawing and the experimental error than is found in this and in some of the other cases here considered may be expected. But to obtain such an agreement the experimental error must be determined by some means more certain than that of the comparison of duplicates. The results of an examination of about ten series of results are now appearing in the *Ber. d. deutsch. chem. Gesel.*

A three-curve drawing, in which a change of curvature comes at the same point, would of course show an error intermediate between the errors of the two-curve and four-curve drawings; whereas, with a three-curve drawing in which the breaks do not come at this point, as in the case where the three curves taken are of equal length, we get a far greater error, namely, 36 times the experimental error (column IV.); and a drawing of as many as even five curves of equal length (column VI.) gives an error eight times greater than it should be.

As far as a two-curve drawing, therefore, the figure may be simplified either with no appreciable increase, or with an actual diminution in the apparent error; but further simplification is impossible, for an attempt to draw it as one curve gives a result of which the total error is many thousand times greater than it ought to be (column II.). The two-curve drawing is, therefore, the simplest, and the only legitimate representation of the experimental values.

The next point examined was whether the two curves in which the figure must be drawn might be made to meet at any point other than 16 per cent. Columns VIII. to XIII. give the results obtained, and show that shifting the meeting-point to even the next experimental point on either side of 16 per cent. increases the total error to from 270 to 20 fold in the various cases, and that the farther it is shifted the more is the error increased.

In all the drawings here mentioned, the four forces applied to the ends of the lath were such that the direction of the curvature was the same throughout (*vide supra*, p. 141); and it was evident that the use of a wavy curve would in some cases produce better concordance. I therefore examined such cases by the application of such curves, and give the results in columns VII., XIV., XV., and XVI.; these results, though considerably better than those given by the other curves, still exhibit errors far too great to permit of the drawings being considered acceptable.

For the mathematical examination, the method which I have employed is the more usual one described by Mr. Lupton (*Phil. Mag.* xxxi. p. 418), but not applied in the way in which he applied it, for that method of application necessitates the employment of several experimental points beyond those which are actually under investigation. I have also introduced one more term into the equations than he did.

If there be  $n$  experimental points, and the values at  $p_1, p_2$ , &c. percentages are  $y_1, y_2$ , &c., then the values for the constants of a parabolic equation of the form  $y = a + bx + cx^2 + dx^3$  may be found from



$$\begin{aligned} na + b \Sigma x + c \Sigma x^2 + d \Sigma x^3 &= \Sigma y, \\ a \Sigma x + b \Sigma x^2 + c \Sigma x^3 + d \Sigma x^4 &= \Sigma xy, \\ a \Sigma x^2 + b \Sigma x^3 + c \Sigma x^4 + d \Sigma x^5 &= \Sigma x^2 y, \\ a \Sigma x^3 + b \Sigma x^4 + c \Sigma x^5 + d \Sigma x^6 &= \Sigma x^3 y^* \end{aligned}$$

In order to simplify the calculations the experimental results were reduced so as to apply exactly to whole numbers, the rate of change being determined by means of the general curve. The maximum correction which had to be applied in any case was less than  $\cdot 05^\circ$ , and any error in applying this must have been quite inappreciable. The reduced values are given in the lower part of Table I.

The results of the examination are given in Table III. When represented by two equations meeting at 16 per cent. we get, as with the graphic method, a total error which is practically identical with the ascertained experimental error —.95 as compared with 1.0 (column III.); whereas an attempt to represent the points by a single equation produces a result with a total error 633 times greater than the experimental error. Columns IV. to IX. show, moreover, that any attempt to alter the position of the change of curvature to either side of 16 per cent., induces a large increase in the total error, and makes this error far too big for the drawing to be considered acceptable: also the farther it is shifted the larger does the error become. The last three columns in the table

\* It may be convenient to quote the following equations: —

$$\begin{aligned} 1 + 2 + 3 \dots + n &= \frac{n(n+1)}{2}, \\ 1^2 + 2^2 + 3^2 \dots + n^2 &= \frac{n(n+1)(2n+1)}{6}, \\ 1^3 + 2^3 + 3^3 \dots + n^3 &= \left\{ \frac{n(n+1)}{2} \right\}^2, \\ 1^4 + 2^4 + 3^4 \dots + n^4 &= \frac{n(n+1)(2n+1)(3n^2+3n-1)}{30}, \\ 1^5 + 2^5 + 3^5 \dots + n^5 &= \frac{n^2(n+1)^2(2n^2+2n-1)}{12}, \\ 1^6 + 2^6 + 3^6 \dots + n^6 &= \frac{n(n+1)(2n+1)(3n^4+6n^3-3n+1)}{42}. \end{aligned}$$

Mr. Hayes has suggested a method by which, when the values of  $x$  differ by unity, the calculation of the constants may often be considerably simplified. If the number of points is odd, we may take the middle point as origin, which gives  $-2, -1, +1, +2$ , &c. as the values for  $y$  of the other points, and the normal equations then become

$$\begin{aligned} na + 2c \Sigma x^2 &= \Sigma y, \\ 2b \Sigma x^2 + 2d \Sigma x^4 &= \Sigma xy, \\ 2a \Sigma x^2 + 2c \Sigma x^4 &= \Sigma x^2 y, \\ 2b \Sigma x^4 + 2d \Sigma x^6 &= \Sigma x^3 y. \end{aligned}$$

The method can also be applied with slight modifications in cases where the number of points is even, or where the constant difference between successive values of  $x$  is not unity.

show the results of an attempt to bridge over the change of curvature at 16 per cent. by a single equation: any four points could be represented with absolute exactness by an equation such as is here used, and yet we cannot get an equation to represent seven of the points in this part of the figure—three on either side of 16 per cent.—without an error twenty-one times greater than is legitimate, and even six or five points cannot be thus represented without this error being five times greater than it should be. This would seem to be quite conclusive that there is a change of curvature here which cannot be smoothed over by any simple equation of this sort.

I have also examined mathematically the portion from 16 to 32 per cent. taken separately, to ascertain the result of representing it by two curves instead of one, and find that such a representation, and also representations in which any six or eight of the nine points are taken, give practically the same total error as a representation of all the nine by one equation—namely, from  $\cdot 021^\circ$  to  $\cdot 025^\circ$ ; so that any splitting up of this portion of the figure is unjustifiable.

Thus it will be seen that the mathematical examination leads to precisely the same conclusion as does the graphic; and for two different methods to lead to the same conclusion as to the existence and position of the breaks must be a strong argument in favour of the reality of these breaks, even if it can be urged that neither of the forms of curves used in the two methods is a really suitable one.

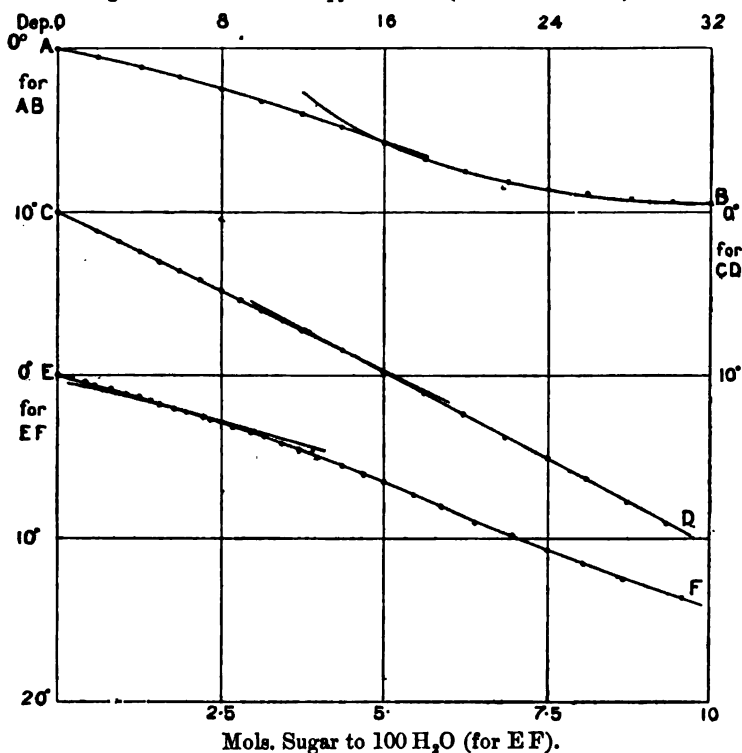
It may be noticed that the errors given by the one method are sometimes larger and sometimes smaller than those given by the other, though their general tenour is always the same. This must inevitably be the case; for the bent-lath curve is not a parabola, and, in addition to this, there are different sources of inaccuracy in the two methods. In the graphic method we have various errors introduced by imperfect plotting, reading, and drawing; while in the mathematical method the curve deduced necessarily makes the sums of the positive and negative errors exactly equal, which, as I have stated above, does not necessarily give us the truest representation.

It is perhaps not altogether unnecessary to correct an erroneous opinion sometimes held, that a change of curvature in a series of freezing-point determinations implies that a different substance or hydrate crystallizes from the solution. This is, of course, not the case: the solvent, water in the present instance, is the crystallizing substance throughout; and the temperature at which ice can be separated from the liquid is as much a continuous property of the solution as is any other property: the breaks in the freezing-point curves are precisely similar to those in the density &c. curves.

Case II.

This is an instance of a break of a very uncertain character, at any rate as to its position. The experimental results are given in Table IV.: they consist of determinations of the depression of the freezing-points of acetic acid by propyl alcohol. The average mean experimental error is  $0^{\circ}\cdot042$ ; but at three points it attains exceptionally large dimensions, and when these three points are omitted we get  $0^{\circ}\cdot029$  as the mean error: when determined by a graphic method which I have described in the *Ber. d. deutsch. chem. Gesel.* xxiv. p. 3332, and xxv. p. 1100,  $0^{\circ}\cdot027$  was obtained as the mean error; and I have taken the mean of these three numbers, namely  $0^{\circ}\cdot033$ , as the most probable value for it.

Fig. 1.—Per cent. of Propyl Alcohol (for AB and CD).



On examination of the figure it appeared to consist of a curve followed by a straight line, the break being at about  
*Phil. Mag.* S. 5. Vol. 33. No. 204. May 1892. 2 H

14.4 per cent. (C D, fig. 1); and such a drawing gives an average apparent error, and also a total error, of  $0^{\circ}.028$ , or .85 times the experimental error (column III. Table V.). Increasing the number of curves used to represent the figure produces scarcely any appreciable diminution of the apparent error till as many as five curves are used (columns IV., V., and VI.); but an attempt to represent it by one curve only (column II.) gives an average apparent error of 0.096, and a total error two hundred times greater than the experimental error (column II.). The two-curve drawing is, therefore, the only acceptable representation.

The curves here mentioned were non-wavy curves, except in the case of the one-curve drawing, and a difficulty arises in the present case in respect to this: for in attempting to extend either portion of the figure beyond the break we get far better concordance by using wavy curves, and, therefore, we ought to use them. But we cannot compare these results with those obtained with a drawing locating the break at 14.4 per cent., unless in this drawing also we use wavy curves. But the substitution of a wavy curve for the straight line in the second part of the figure is evidently (to my mind) unjustifiable, for it follows the points more closely than the experimental error in this region justifies. For the sake of comparison with the results obtained by parabolic equations with four constants, it is also necessary to use wavy curves. The only thing to be done, therefore, is to use them throughout, bearing in mind that they give errors which are too small: the use of such curves, moreover, masks the precision of the break to a very large extent; for the first portion of the figure cannot be extended at all beyond 14.4 per cent. by a non-wavy curve without a considerable increase of error, although as far as this point such a curve gives just as good results as a wavy one.

The results given in columns VII. to XV. show that there is an increase of error on attempting to make the break occur at any point other than about 14 per cent., although the increase is but small in the cases where it is moved to 16 or 18 per cent.

Table VI. contains the results of the mathematical examination. Both as to the good results obtained by two equations (which are comparable with those in column XI. Table II.); the impossibility of using only one equation; and the increase in the error when the position of change is shifted to either side of 14.4 per cent.—very small at first but increasing with the distance to which it is shifted—the general tenour of the results is the same as that of those obtained by the graphic method—a break at about 14 per

cent., with a possible error of several units per cent., which error would, however, be considerably diminished if we were not using equations and curves of a complexity greater than the results seem to justify.

In the case of a feebly marked break of this sort, a single equation will, naturally, bridge it over for a considerable distance; but the results in columns x. and xi. show that a single curve of the same length as those which I consider represent the results cannot be applied to this part of the figure without increasing the apparent error, and even if there were no increase in such a case, it must be remembered that this representation could not be accepted, for it would necessitate the use of three equations to represent the whole of the figure, whereas two are sufficient, and give results in good accord with the experimental error.

It may be mentioned that the position of this break (14.4 per cent.) corresponds to an exact molecular proportion,  $C_2H_6O_2 : 6C_2H_4O_2$ , requiring 14.3 per cent. This is the only break amongst those investigated in the present communication in which the proportion of dissolved substance is sufficiently large to admit of any statement as to the indication of definite molecular proportions.

### Case III.

The freezing-points of aqueous solutions of cane-sugar were the subject of investigation in this case, and the experimental values have already been published in the *Berichte der deutsch. chem. Gesel.* (xxiv. p. 3333), together with some details of an examination both by the graphic and mathematical methods. The two methods were found to agree most fully in showing that one parabolic or bent-lath curve cannot represent the results, but that two such curves, meeting at 2 to 2.5 molecules to  $100H_2O$  (see E F, fig. 1), would do so. The experimental error was found to be  $0.023^\circ$ , and the apparent errors of the representation were as follows:—

	Graphic Method.	Math. Method.
Drawn as 1 curve	$e_1$ ..... $0.058^\circ$	$0.054^\circ$
	E..... $39.15^\circ$	$9.5^\circ$
	Rel. error 1700	413
" 2 curves meeting at 2.5 mols.	$e$ ..... $0.0250^\circ$	$0.0193^\circ$
	E..... $0.0270^\circ$	$0.0257^\circ$
	Rel. error 1.2	1.1
	2 H 2	

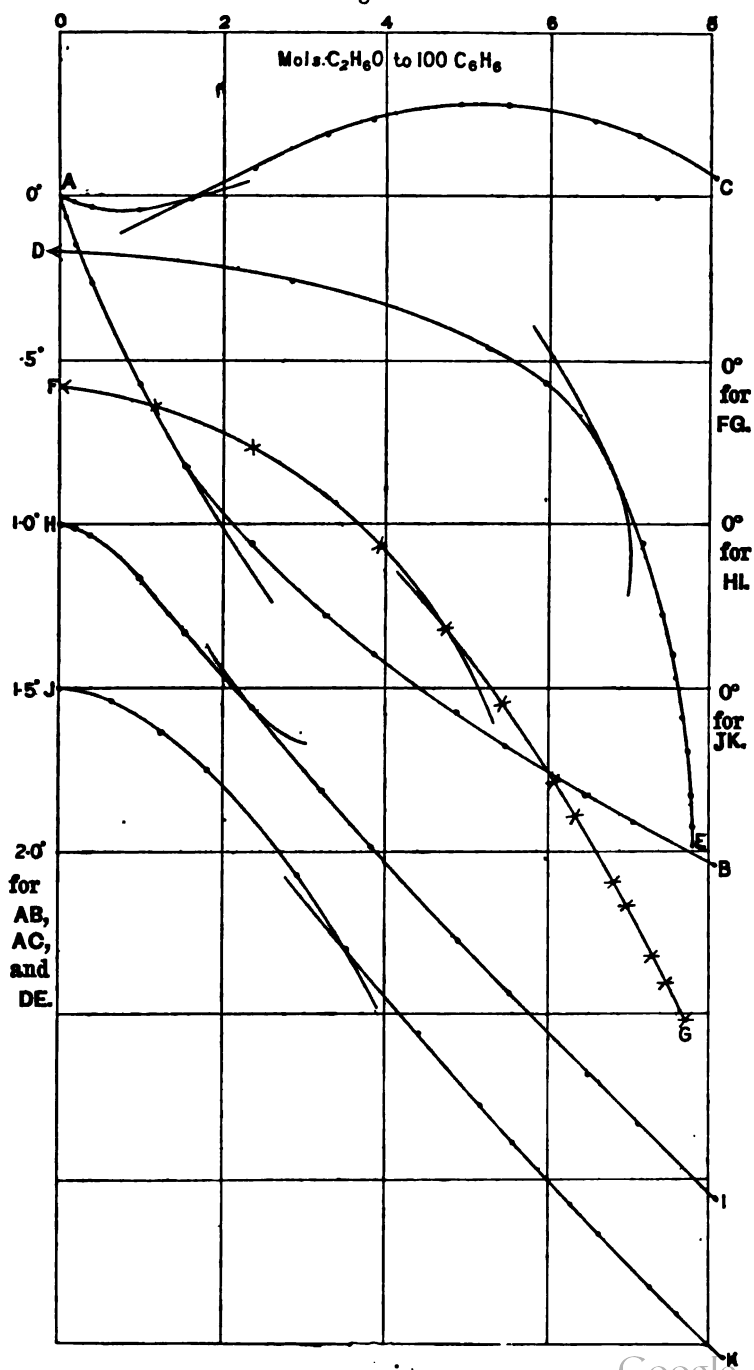
In Table VII. I have given the results obtained by the Graphic method when sections of different length, starting from the lower end, are drawn as one curve. Thus when only  $\frac{1}{10}$  of the whole figure are drawn in one section (column VIII.) the average error is only very slightly too small; it becomes practically identical with the experimental error when  $\frac{2}{10}$  of the figure are taken (column VII.), and the length of the section taken may be increased to  $\frac{1}{10}$ ,  $\frac{2}{10}$ , and even  $\frac{3}{10}$  of the whole (columns VI., V., and II.) without any appreciable increase in this error; whereas as soon as a particular point is passed, an increase in the length of the section taken involves a rapid increase in the apparent error, so that the remaining  $\frac{1}{10}$  of the figure cannot be included in the drawing without giving an average apparent error 2.6 times greater than it should be. The average error,  $e_1$ , has alone, as will be seen, been considered in this case, and the numbers would have been far more striking if the total errors had been taken\*, but, even without taking these, the results afford a striking illustration that the breaking up of a figure into separate sections, when examined by the lath, is by no means analogous to the splitting up of a figure into separate sections of any unsuitable form, which necessarily shows a gradually decreasing concordance with the experimental points as the lengths of the separate sections are increased: here we find practically no decrease till a certain length is reached, and then there is a rapid decrease. The break in the case of these results is, moreover, one which I should by no means term very well marked.

#### Case IV.

This is an instance of a break between two curves of which the curvature (in the form of plotting used) is in the same direction. The experimental results (Table VIII.) refer to the depression of the freezing-point of benzene by ethyl alcohol. Two entirely different samples of alcohol (one of which was prepared in Prof. van t'Hoff's laboratory) were used, the determination with this latter sample being marked by an asterisk in the table. The two series agree very closely together, although the solutions in the case of one of them were not made up with very great exactness. The mean

\* For the two-curve drawing, with a break at 2 mols., the total error is 1.27 times the experimental error; for the one-curve drawing (column III.) it is 4.25 times, and for a one-curve drawing from 1 molecule downwards (column IV.) it is 4.3 times the experimental error.

Fig. 2.



experimental error determined by the graphic method was  $0\cdot0021^\circ$ ; and a two-curve drawing, such as that shown in fig. 2, AB, gives a mean apparent error, and also total error, of almost exactly this amount, namely,  $\cdot0020$  (column x., Table VIII.), but an attempt to represent the results as a single curve increases the apparent error to 5 times, and the total error to 219 times the known experimental error.

The examination by the mathematical method shows that two parabolas will represent the results with nearly as close an agreement with the experimental error (1.5 times this error\*) as two bent-lath curves do, but that a single parabola is even more inapplicable than a single bent-lath curve, the total apparent error according to it being no less than 3380 times greater than the experimental error.

Some little doubt was entertained at first as to the exact position of the break in this case, chiefly owing to the difficulty of getting a lath of a flexibility, and sectional paper of a size and accuracy, suited to the curvature of the figure and to the experimental error, so the values were manipulated in a variety of ways, and the results form a striking illustration of how independent the recognition of a true break is of the nature of the ordinates and abscissæ selected for the plotting, for all the figures illustrated in fig. 2 concur in placing a break at the same point,  $0\cdot8^\circ$ , in spite of the great dissimilarity of their general form. The various plottings are:—

A B. Depression against molecular composition.

Depression against percentage composition gives a very similar figure.

A C. Depression *minus* the readings of a selected parabola against molecular composition. (A depression of  $8^\circ$  becomes  $0^\circ$  according to this plotting.)

D E. Depression against the reciprocal of the molecular composition.

F G. Depression against the logarithm of the molecular composition.

H I. Half the square of the depression against the molecular composition.

J K. Depression against the square root of the molecular composition.

The numbers given at the top of the figure refer to A B and A C only. In the case of H I only should there, I think, be

\* The excess in this case may be due to some small error, of which there are indications, but which I cannot locate, in the equation for the second portion of the result.



any doubt as to the position of the break ; by using a non-wavy curve for the first portion of the figure in this case the break might be made to occur at the experimental point next above that shown for its position in the figure.

The particular figure which was selected for the graphic and mathematical examination is, it will be noticed, the one which exhibits the greatest seeming regularity, and which would appear most favourable for representation by a single curve.

The instances here detailed will, I trust, be sufficient to show the very strong nature of the evidence as to the reality of these changes of curvature : that the recognition of them is certainly not a mere matter of taste on the part of the draughtsman, even in the case of feebly marked breaks, and that the deduction of parabolas from the experimental results themselves tends to precisely the same conclusions as the much more expeditious method of examining the results with a flexible lath. At the same time I trust that the present communication will show that the application of the graphic method requires a great amount of care and a close attention to experimental and other considerations, and it is to be feared that the hurried use of it by those who have not taken the trouble to master the necessary details, or to acquire the requisite amount of skill, may bring it into undeserved disrepute.

It must be remembered, of course, that a bent-lath curve is not necessarily suited to every curvilinear figure, any more than is a section of a parabola ; but as far as my experience goes the application of a bent lath to a curvilinear figure differing materially from a bent-lath curve (such as a large portion of an hyperbola) would not lead to wrong conclusions, but simply to no conclusions at all. In such a case we find that the error of the drawing increases regularly with the length of the figure drawn in one section, and that any supposed breaks to which we may have been erroneously led by the examination will be found to be false when the method of plotting is altered so as to obtain a figure of a different character.

October 1891.

TABLE I.—Depression of the Freezing-Point of Water by Propyl Alcohol.

## Experimental Results.

Per cent.	Depression.	Mean error.	Per cent.	Depression.	Mean error.
2.027	$\left\{ \begin{smallmatrix} .615 \\ .605 \end{smallmatrix} \right\}$ .610	-.0050	17.902	$\left\{ \begin{smallmatrix} 6.702 \\ 6.580 \end{smallmatrix} \right\}$ 6.641	-.0610
3.974	$\left\{ \begin{smallmatrix} 1.199 \\ 1.199 \end{smallmatrix} \right\}$ 1.199	0	19.892	$\left\{ \begin{smallmatrix} 7.582 \\ 7.443 \end{smallmatrix} \right\}$ 7.513	-.0645
5.867	$\left\{ \begin{smallmatrix} 1.851 \\ 1.860 \end{smallmatrix} \right\}$ 1.856	-.0045	21.884	$\left\{ \begin{smallmatrix} 8.108 \\ 8.047 \end{smallmatrix} \right\}$ 8.078	-.0305
7.915	$\left\{ \begin{smallmatrix} 2.582 \\ 2.597 \end{smallmatrix} \right\}$ 2.591	-.0075	23.871	$\left\{ \begin{smallmatrix} 8.614 \\ 8.485 \end{smallmatrix} \right\}$ 8.550	-.0645
10.025	$\left\{ \begin{smallmatrix} 3.246 \\ 3.254 \end{smallmatrix} \right\}$ 3.250	-.0040	25.935	$\left\{ \begin{smallmatrix} 8.813 \\ 8.819 \end{smallmatrix} \right\}$ 8.816	-.0030
11.917	$\left\{ \begin{smallmatrix} 3.989 \\ 3.997 \end{smallmatrix} \right\}$ 3.993	-.0040	27.891	$\left\{ \begin{smallmatrix} 9.137 \\ 9.060 \end{smallmatrix} \right\}$ 9.098	-.0385
13.968	$\left\{ \begin{smallmatrix} 4.782 \\ 4.756 \end{smallmatrix} \right\}$ 4.769	-.0130	29.902	$\left\{ \begin{smallmatrix} 9.216 \\ 9.187 \end{smallmatrix} \right\}$ 9.202	-.0145
15.925	$\left\{ \begin{smallmatrix} 5.543 \\ 5.581 \end{smallmatrix} \right\}$ 5.562	-.0190	31.878	$\left\{ \begin{smallmatrix} 9.449 \\ 9.469 \end{smallmatrix} \right\}$ 9.459	-.0100
2	.601		18	6.688	
4	1.207		20	7.553	
6	1.900		22	8.109	
8	2.620		24	8.673	
10	3.241		26	8.822	
12	4.025		28	9.101	
14	4.782		30	9.212	
16	5.601		32	9.469	

TABLE II.—Depression of the Freezing-Point of Water by Propyl Alcohol, examined by the Graphic Method.  
(Average Experimental Error = .0215°.)

I. p. Per cent. Alcohol.	Apparent Errors when drawn as							Apparent Error when drawn as two Curves meeting at									
	II. 1 Curve.	III. 2 Curves meeting at 16 per cent.	IV. 3 Curves meeting at 11 and 22 per cent.	V. 4 Curves meeting at 8, 16, and 24 per cent.	VI. 5 Curves meeting at 6.5, 13, 19.5, and 26 per cent.	VII. 1 Wavy Curve.	VIII. 10 per cent.	IX. 12 per cent.	X. 14 per cent.	XI. 18 per cent.	XII. 20 per cent.	XIII. 22 per cent.	Wavy Curves.				
													XIV. 10 per cent.	XV. 12 per cent.	XVI. 14 per cent.		
3.027	+ .10	+ .01	0°	0°	0°	0°	0°	0°	0°	0°	- .02	+ .01	0°	0°	0°		
3.974	+ .21	+ .05	+ .02	+ .03	+ .03	+ .04	...	...	...	+ .01	0°	+ .06	...	...	...		
5.867	+ .23	- .02	- .04	- .01	- .03	+ .01	...	...	...	- .03	- .05	0°	...	...	...		
7.915	+ .22	- .07	- .09	- .08	- .07	+ .03	...	...	...	- .08	- .07	- .02	...	...	...		
10.025	+ .34	+ .04	+ .04	+ .05	+ .07	+ .20	+ .12	...	...	+ .05	+ .07	+ .12	...	...	...		
11.917	+ .21	- .01	+ .04	- .01	+ .01	+ .20	+ .30	...	...	+ .02	+ .02	+ .04	...	...	...		
13.868	+ .12	- .01	+ .12	+ .02	+ .02	+ .23	+ .46	...	...	+ .04	+ .06	+ .04	...	...	...		
15.925	0	0	+ .16	0	+ .08	+ .20	+ .46	...	...	+ .09	+ .11	+ .03	...	...	...		
17.902	- .41	- .03	- .11	+ .02	- .10	- .16	+ .06	...	...	- .17	- .10	- .21	...	...	...		
19.892	- .66	- .02	- .16	- .01	- .01	- .32	- .22	...	...	- .10	- .04	- .24	...	...	...		
21.894	- .80	+ .02	- .01	+ .04	+ .02	- .28	- .23	...	...	- .08	- .14	- .09	...	...	...		
23.871	- .46	- .02	- .03	- .01	- .01	- .25	- .25	...	...	...	- .18	- .13	...	...	...		
25.835	- .05	+ .03	+ .03	+ .01	+ .01	- .10	- .14	...	...	...	- .08	- .02	...	...	...		
27.891	+ .24	- .02	- .03	- .04	- .03	+ .11	- .10	...	...	...	- .10	...	...	...	...		
29.902	+ .72	- .04	+ .05	+ .05	+ .06	- .02	+ .05	...	...	...	+ .04	+ .07	...	...	...		
31.878	+ .106	- .04	- .05	- .04	- .03	- .18	0	...	...	...	- .02	- .04	...	...	...		
Sum.....	+ .345	+ .20	+ .45	+ .22	+ .30	+ .101	+ .145	+ .92	+ .53	+ .21	+ .26	+ .40	+ .33	+ .48	+ .30		
	- .218	- .20	- .51	- .15	- .28	- .132	- .094	- .62	- .38	- .26	- .28	- .47	- .37	- .39	- .24		
4.....	.352	.0275	.060	.023	.036	.146	.199	.140	.081	.062	.054	.079	.068	.078	.068		
5.....	.145	1	13	1	4.8	51	78	47	25	10	11	21	13	18	12		
6.....	.73	1	1	1	1	6	4.1	3.4	2.8	1.6	1.6	1.4	1.2	2.6	1		
7.....	.872	.0275	.780	.023	.173	44.68	64.4	23.7	6.99	1.832	1.950	2.318	.905	3.560	.696		
Bel. error ...	1.7377 *	1.28 *	36 *	1.07 *	8 *	2078 *	2694†	987†	270†	20†	25†	73†	38†	156†	29†		

\* Compared with the experimental error as unity.  
† Compared with the total error (E) of the same portion of the figure when it is drawn as two curves meeting at 16 per cent. (col. III.)

TABLE III.—Depression of the Freezing-Point of Water by  
Mathematical  
(Average Experimental

I. P. Per cent. Alcohol.	When represented by		When represented by		
	II. 1 Equa- tion.	III. 2 Equa- tions meeting at 16 per cent.	IV. 10 per cent.	V. 12 per cent.	VI. 14 per cent.
2	— 0	— 0	0	0	0
4	— 009	— 001	.....	.....	.....
6	— 053	+ 022	.....	.....	.....
8	— 052	— 014	.....	.....	.....
10	— 022	— 049	.....	.....	.....
12	+ 143	+ 043	— 042	.....	.....
14	+ 164	0	+ 029	— 097	.....
16	+ 214	+ 011	+ 134	+ 159	— 109
18	+ 186	{ — 012 } — 005	+ 160	+ 249	+ 190
20	— 144	+ 015	— 121	— 036	+ 027
22	— 303	— 021	— 240	— 201	— 088
24	— 222	+ 023	— 132	— 159	— 048
26	— 196	— 020	— 038	— 125	— 051
28	+ 061	+ 024	+ 145	+ 026	+ 046
30	+ 106	— 040	+ 148	+ 048	+ 017
32	+ 178	+ 036	+ 148	+ 143	+ 079
	— 052	— 011	— 192	— 003	— 061
Sum..... {	+ 1052 — 1053	+ 174 — 173	+ 764 — 765	+ 625 — 620	+ 359 — 357
$e_1$ .....	1316	0204	128	113	072
$e_2$ .....	38.3	1	40	36	15.3
$e_3$ .....	2.70	1	1.95	1.8	1.25
$E$ .....	13.608	0204	9.99	7.32	1.377
Rel. error ...	633 *	0.95 *	499†	407†	69†

\* Compared with the experimental error as unity.

† Compared with the total error (E) of the same portion of the

Constants of the Equations,  $x=2p$ . The starting-

p.	a.	b.	c.	d.
0 to 32	.....	48111	053856	— 0029464
0 " 16	.....	586112	014257	— 0000237
16 " 32	5.5959	1.26382	— 164645	+ 008376
10 " 32	3.1991	8448	01410	— 003697
12 " 32	3.9275	1.06653	— 053527	0002253
14 " 32	4.6728	1.2209	— 10647	003253

Propyl Alcohol : Apparent Errors when examined by the Method.

Error =  $\cdot 0215^\circ$ .)

two Equations meeting at			When represented by one Equation from		
VII.	VIII.	IX.	X.	XI.	XII.
18 per cent.	20 per cent.	22 per cent.	10 to 22 per cent.	12 to 22 per cent.	12 to 20 per cent.
$+\cdot 011$	$+\cdot 035$	$-\cdot 017$			
$+\cdot 029$	$+\cdot 057$	0			
$-\cdot 021$	$-\cdot 002$	$-\cdot 033$			
$-\cdot 069$	$-\cdot 071$	$-\cdot 058$			
$+\cdot 018$	$-\cdot 006$	$+\cdot 051$	$+\cdot 038$		
$-\cdot 013$	$-\cdot 056$	$+\cdot 030$	$-\cdot 088$	$+\cdot 009$	$+\cdot 011$
$+\cdot 035$	$-\cdot 018$	$+\cdot 067$	$-\cdot 001$	$-\cdot 043$	$-\cdot 043$
$+\cdot 082$	$+\cdot 036$	$+\cdot 072$	$+\cdot 116$	$+\cdot 072$	$+\cdot 059$
$-\cdot 072$	$-\cdot 088$	$-\cdot 163$	$-\cdot 036$	$-\cdot 025$	$-\cdot 037$
.....	$+\cdot 115$	$-\cdot 148$	$-\cdot 062$	$-\cdot 019$	$+\cdot 009$
.....	.....	$+\cdot 201$	$+\cdot 033$	$+\cdot 007$	
$+\cdot 175$	$+\cdot 243$	$+\cdot 421$	$+\cdot 187$	$+\cdot 088$	$+\cdot 079$
$-\cdot 175$	$-\cdot 241$	$-\cdot 419$	$-\cdot 187$	$-\cdot 087$	$-\cdot 080$
$\cdot 039$	$\cdot 048$	$\cdot 075$	$\cdot 053$	$\cdot 029$	$\cdot 032$
4.7	8.0	19	9.1	2.25	1.95
1	4.45	1.4	1	1	1
$\cdot 183$	1.710	1.997	$\cdot 482$	$\cdot 065$	$\cdot 062$
11†	95†	111†	21†	5.0†	4.5†

figure when it is drawn as two curves meeting at 16 per cent. (col. III.)

point of the Equation is taken as its origin.

p.	a.	b.	c.	d.
0 to 18	.....	$\cdot 6085$	$\cdot 001909$	$\cdot 001352$
0 " 20	.....	$\cdot 64752$	$\cdot 011618$	$\cdot 002373$
0 " 22	.....	$\cdot 56452$	$\cdot 019959$	$-\cdot 000236$
10 " 22	3.2791	$\cdot 53400$	$\cdot 13975$	$-\cdot 015614$
12 " 22	4.0338	$\cdot 53333$	$\cdot 20087$	$-\cdot 028856$
12 " 20	4.0362	$\cdot 5440$	$\cdot 18379$	$-\cdot 024864$

TABLE IV.—Depression of the Freezing-Point of Acetic Acid by Propyl Alcohol.

## Experimental Results.

Per cent. Alcohol.	Depression.	Mean error.	Per cent. Alcohol.	Depression.	Mean error.
2.001	$\left\{ \begin{smallmatrix} 1.254 \\ 1.283 \end{smallmatrix} \right\}$ 1.259	.005	16.114	$\left\{ \begin{smallmatrix} 9.750 \\ 9.763 \end{smallmatrix} \right\}$ 9.757	.007
2.936	$\left\{ \begin{smallmatrix} 1.814 \\ 1.831 \end{smallmatrix} \right\}$ 1.822	.009	18.089	$\left\{ \begin{smallmatrix} 11.082 \\ 11.155 \end{smallmatrix} \right\}$ 11.119	.037
4.063	$\left\{ \begin{smallmatrix} 2.525 \\ 2.541 \end{smallmatrix} \right\}$ 2.533	.008	20.166	$\left\{ \begin{smallmatrix} 12.394 \\ 12.471 \end{smallmatrix} \right\}$ 12.433	.039
5.028	$\left\{ \begin{smallmatrix} 3.142 \\ 3.153 \\ 3.133 \end{smallmatrix} \right\}$ 3.143	.004	22.141	$\left\{ \begin{smallmatrix} 13.840 \\ 13.732 \end{smallmatrix} \right\}$ 13.786	.054
5.974	$\left\{ \begin{smallmatrix} 3.723 \\ 3.615 \\ 3.641 \end{smallmatrix} \right\}$ 3.660	.033	24.108	$\left\{ \begin{smallmatrix} 14.783 \\ 15.021 \\ 15.267 \\ 14.828 \\ 14.722 \end{smallmatrix} \right\}$ 15.020	.109
7.031	$\left\{ \begin{smallmatrix} 4.356 \\ 4.260 \end{smallmatrix} \right\}$ 4.308	.048	26.143	$\left\{ \begin{smallmatrix} 16.829 \\ 16.165 \\ 16.606 \\ 16.198 \\ 16.202 \end{smallmatrix} \right\}$ 16.400	.135
8.066	$\left\{ \begin{smallmatrix} 4.861 \\ 4.902 \\ 5.015 \end{smallmatrix} \right\}$ 4.926	.046	28.149	$\left\{ \begin{smallmatrix} 17.624 \\ 17.622 \\ 17.863 \\ 18.130 \\ 18.076 \end{smallmatrix} \right\}$ 17.863	.107
9.077	$\left\{ \begin{smallmatrix} 5.570 \\ 5.506 \end{smallmatrix} \right\}$ 5.538	.032	30.198	$\left\{ \begin{smallmatrix} 19.230 \\ 19.217 \\ 19.117 \\ 19.231 \end{smallmatrix} \right\}$ 19.202	.030
10.067	$\left\{ \begin{smallmatrix} 6.111 \\ 6.103 \\ 6.062 \end{smallmatrix} \right\}$ 6.095	.015			
12.100	$\left\{ \begin{smallmatrix} 7.473 \\ 7.313 \\ 7.367 \\ 7.256 \end{smallmatrix} \right\}$ 7.352	.046			
14.043	$\left\{ \begin{smallmatrix} 8.395 \\ 8.486 \\ 8.365 \\ 8.513 \end{smallmatrix} \right\}$ 8.440	.035			
2	1.259		14	8.415	
3	1.861		16	9.681	
4	2.494		18	11.067	
5	3.128		22	12.322	
6	3.675		20	13.692	
7	4.289		24	14.948	
8	4.886		26	16.304	
9	5.492		28	17.764	
10	6.055		30	19.069	
12	7.293				

TABLE V.—Depression of the Freezing-Point of Acetic Acid by Propyl Alcohol, examined by the Graphic Method. (Mean Experimental Error = 0.035°.)

I. P. Per cent. Alcohol.	Apparent error according to a drawing as						Apparent error when drawn as two curves meeting at									
	II. 1 curve.	III. 2 curves meeting at 14.4 per cent.	IV. 3 curves meeting at 10 & 20 per cent.	V. 4 curves meeting at 7.5, 15 & 22.5 per cent.	VI. 5 curves meeting at 6, 12, 18, & 24 per cent.	VII. 6 per cent.	VIII. 8 per cent.	IX. 10 per cent.	X. 12 per cent.	XI. 14 per cent.	XII. 16 per cent.	XIII. 18 per cent.	XIV. 20 per cent.	XV. 22 per cent.		
2.001	-.08	0	0	0	-.02	0	0	0	-.01	0	-.01	0	-.01	0	+.01	+.01
2.996	-.03	+.01	+.02	+.02	+.02	...	...	...	...	+.01	+.01	+.02	+.01	+.01	+.01	+.01
4.033	-.07	0	-.02	-.02	0	...	...	...	...	0	-.02	-.05	-.02	-.03	...	...
5.028	-.08	-.05	-.02	-.05	0	+.02	...	...	...	-.05	0	+.02	-.05	-.07	-.07	...
5.974	-.04	+.01	+.05	+.01	+.02	-.01	...	...	...	+.01	0	+.02	+.02	+.01	+.01	...
7.031	-.02	0	0	0	+.01	0	0	...	...	-.01	-.01	+.01	+.01	+.01	0	0
8.066	0	+.01	0	+.02	-.02	-.03	-.03	...	...	+.01	-.02	-.01	-.01	+.01	-.01	0
9.077	0	-.01	-.02	0	0	0	0	...	...	+.01	+.01	+.01	+.01	+.01	0	0
10.067	+.10	+.04	+.02	+.03	+.03	-.02	-.03	+.02	-.10	+.04	+.03	+.02	+.02	+.02	+.05	+.05
12.100	+.10	+.01	+.02	-.01	0	0	0	...	...	-.01	-.04	+.03	+.03	+.01	+.02	+.02
14.043	+.23	+.01	+.02	+.02	0	+.05	+.08	+.10	+.07	+.01	+.04	+.06	+.09	+.10	+.03	+.03
16.114	+.23	+.03	+.03	+.02	+.02	+.04	+.05	+.06	+.06	+.05	+.03	0	+.01	+.01	+.03	+.03
18.089	+.10	-.05	-.10	-.05	+.01	-.05	-.05	-.05	-.03	-.03	...	...	...	...	-.06	-.06
20.166	+.07	+.02	+.02	-.02	0	-.02	+.01	+.02	+.02	+.03	...	...	...	...	+.01	+.01
22.141	-.02	0	-.08	-.04	-.09	-.05	-.02	-.02	-.02	-.01	...	...	...	...	...	...
24.108	+.03	+.12	+.04	+.04	-.02	+.06	+.07	+.08	+.06	+.07	...	...	...	...	...	...
26.143	+.08	+.07	+.02	+.02	+.02	+.10	+.02	+.02	+.02	+.08	...	...	...	...	...	...
28.149	-.26	-.07	-.09	-.05	-.04	+.03	-.10	-.09	-.06	-.08	...	...	...	...	...	...
30.196	-.30	-.03	0	+.03	0	+.13	-.05	-.04	+.04	-.02	...	...	...	...	...	...
Sum .....	+.86	+.32	+.22	+.21	+.14	+.43	+.24	+.26	+.27	+.25	+.11	+.14	+.18	+.24	+.24	+.24
$\epsilon_1$ .....	-.96	-.22	-.36	-.24	-.19	-.23	-.28	-.21	-.21	-.21	-.16	-.18	-.21	-.27	-.27	-.27
$\epsilon_2$ .....	-.08	-.028	-.031	-.024	-.017	-.044	-.040	-.043	-.048	-.024	-.026	-.025	-.028	-.034	-.034	-.034
$\epsilon_3$ .....	14.3	1	1	1	1	2.0	1.2	2.0	1.15	1	1	1	1.1	1.26	1.26	1.26
$\epsilon_4$ .....	4.6	1	1	1	1	1	1	1	1	1	1	1	1	1.2	1.2	1.2
$\epsilon_5$ .....	6.59	-.028	0.31	-.024	-.017	-.086	-.048	-.038	-.055	-.024	-.025	-.025	-.031	-.051	-.051	-.051
Rel. error ...	200*	0.88*	0.94*	0.73*	0.52*	3.5†	1.7†	2.6†	1.7†	(1)	1.25†	1.1†	1.6†	2.8†	2.8†	2.8†

\* Compared with the experimental error as unity.  
† Compared with the total error,  $\epsilon_5$ , of the same portion of the figure when it is drawn as two curves meeting at 14 per cent. (col. XI.).

TABLE VI.—Depression of the Freezing-Point of Acetic Acid  
Mathematical  
Mean Experimental

I. <i>p.</i> Per cent. Alcohol.	When represented by		When represented by		
	II. 1 Equa- tion.	III. 2 Equa- tions meet- a little be- yond 14.	IV. 8 per cent.	V. 10 per cent.	VI. 12 per cent.
2	-.015	-.003	0	0	0
3	-.002	+.013	.....	.....	.....
4	-.023	-.007	.....	.....	.....
5	-.046	-.032	.....	.....	.....
6	+.011	+.022	.....	.....	.....
7	+.001	+.007	.....	.....	.....
8	+.008	+.006	-.047	.....	.....
9	+.005	-.007	-.077	.....	.....
10	+.045	+.021	-.053	+.007	.....
12	+.016	-.039	-.084	-.046	-.023
14	+.111	+.015	+.040	+.055	+.051
16	+.076	+.035	+.053	+.042	+.030
18	-.061	-.047	-.029	-.057	-.071
20	-.042	+.010	+.041	-.003	-.010
22	-.110	-.037	+.009	-.044	-.041
24	-.029	+.042	+.098	+.045	+.056
26	-.009	+.036	+.092	+.046	+.059
28	-.040	-.058	-.031	-.050	-.044
30	+.115	+.022	-.007	+.012	-.004
Sum .....	+ .338	+ .230	+ .333	+ .207	+ .196
	-.377	-.230	-.328	-.200	-.193
$e_1$ .....	.040	.024	.051	.037	.039
$e_2$ .....	2.35	1	2.0	1	1
$e_3$ .....	8.3	1	2.2	1	1
$E$ .....	1.494	.024	.292	.037	.039
Rel. error ...	45 *	0.73 *	10.1†	1.1†	1.2†

\* Compared with the experimental error as unity.

† Compared with the total error ( $E$ ) of the same portion of the

## Constants of the

<i>p.</i>	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
0 to 30	.....	1.2545	-.011216	.0008564
0 „ 14	.....	1.2696	-.014712	.0007683
16 „ 30	9.7164	1.2995	.00352	.0003054
8 „ 30	4.8394	1.1376	.025677	-.0010504
10 „ 30	6.0617	1.16514	.020853	-.0007175
.....	.....	.....	.....	.....



by Propyl Alcohol: Apparent Error when examined by the Method.

Error = 0.033°.

two Equations meeting at			By one Equation from	
VII.	VIII.	IX.	X.	XI.
16 per cent.	18 per cent.	2 per cent.	6 to 20 per cent.	7 to 22 per cent.
-001	+006	-005		
+015	+022	+012		
-006	-002	-011		
-032	-030	-037		
+020	+017	+015	+002	
+004	-002	-001	+035	-004
+003	-009	-002	-004	-011
-010	-023	-012	-040	-025
+020	+007	+021	-024	+005
-032	-037	-018	-072	-035
+039	+057	+073	+034	+062
-020	+042	+045	+030	+042
.....	-047	-070	-063	-061
.....	.....	-012	+002	+009
.....	.....	.....	.....	+016
+101	+161	+166	+203	+136
-099	-160	-168	-203	-134
017	025	024	024	027
1	1	1	1.3	1
1	1	1	1.6	1
017	025	024	050	027
1†	1.3†	1.3†	2.4†	1.2†

figure when drawn as two curves meeting at about 14 per cent. (col. III.).

Equations,  $x = 2p$ .

p.	a.	b.	c.	d.
12 to 30	7.2697	1.1693	-028498	-0014221
0 " 16	.....	1.2751	-018061	-0012061
0 " 18	.....	1.2886	-025409	-0020310
0 " 20	.....	1.2742	-019249	-0014920
6 " 20	8.7774	1.0815	-023862	-0005630
7 " 22	4.2854	1.1792	-000605	-0012653

TABLE VII.—Depression of the Freezing-Point of Water by Cane-Sugar.

Examined by the Graphic Method.

Experimental error =  $0.023^{\circ}$ .

I. Mols. Sugar to 100 H <sub>2</sub> O.	II. As 2 curves meeting at 2 mols.	III. 0 mol.	IV. 1 mol.	As one curve from			
				V. 3 mols.	VI. 4 mols.	VII. 5 mols.	VIII. 6 mols.
.19	0	-01	0	0	0	0	0
.36	0	-03					
.57	+0	-06					
.83	+010	-05					
1.04	-015	-09	-.025				
1.19	+015	-05	0				
1.35	-015	-09	-.040				
1.50	-030	-10	-.050				
1.70	-035	-09	-.065				
1.85	+035	-03	+005				
1.99	-005	-05	-.030				
2.30	-010	-01	-.010				
2.40	+005	0	+010				
2.63	+025	+05	+035				
2.88	+010	+05	+030				
3.13	+010	+07	+055	+015			
3.40	-020	+06	+015	-015			
3.67	-015	+08	+015	0			
4.00	+015	+10	+055	+035	+015		
4.34	-045	+03	-.005	-.035	-.050		
4.67	+010	+08	+025	+030	+015		
5.05	0	+05	+015	+005	+005	+020	
5.40	-045	-02	-.025	-.035	-.035	-.015	
5.86	+060	+05	+065	-.050	+060	+085	
6.37	-030	-11	-.040	-.045	-.040	-.035	-.035
6.98	0	-10	-.005	0	0	-.005	+015
7.53	-.005	-12	-.020	-.030	-.010	-.025	-.010
8.10	+095	-03	+080	+080	+095	+070	+080
8.72	-.065	-14	-.060	-.060	-.060	-.080	-.080
9.56	-.050	+01	+010	+010	-.025	-.030	0
Sum ... {	+290 -385	+91 -84	+405 -375	+225 -220	+190 -220	+175 -195	+095 -125
$\epsilon_1$ .....	.0225	.058	.030	.030	.034	.041	.037
Rel. error*	1	2.6	1.15	0.96	0.98	1.06	.090

\* Relative value of  $\epsilon_1$  (not the total error) compared with that of the same portion of the figure when drawn as two curves meeting at 2 mols. (col. II.).

TABLE VIII.—Depression of the Freezing-Point of Benzene by Ethyl Alcohol.  
Mean Experimental Error = 0.0021°.

Alcohol per cent.	Mols. Alcohol to 100C <sub>6</sub> H <sub>6</sub> .	Log. Mols.	$\sqrt{\text{Mols.}}$	$\frac{1}{\text{Mols.}}$	Depression.	$\frac{(\text{Dep.})^2}{2}$ .	Dep. - $y$ .†	Errors by Graphic Method.		Errors by Mathematical Method.	
								1 Curve. IX.	2 Curves. X.	1 Equa- tion.† XI.	2 Equa- tions.§ XII.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.				
-0.280	-0.474	2.6738	21.77	21.097	-0.351	-0.006	+0.077	+0.060	-0.020	-0.039	+0.012
-1.171	-1.986	1.2080	4.56	5.0353	-1.373	-0.094	+0.238	+0.125	-0.025	-0.095	-0.010
-2.297	-3.901	1.5912	62.46	2.5634	-2.510	-0.315	+0.811	+0.175	+0.045	-0.072	+0.041
-3.797 *	-9.878	1.9947	99.39	1.0124	-5.698	-1.623	+0.863	-0.025	+0.030	-0.051	-0.028
-9.134	1.5510	0.1906	1.2454	6.448	-81.86	-3.351	+0.155	-0.150	0	-0.066	+0.009
1.3622 *	2.3395	0.3691	1.5296	4.334	1.0554	5.570	-0.829	-0.075	+0.005	+0.297	-0.053
1.8920 *	3.2671	0.5142	1.8075	3.161	1.2823	8.222	-1.874	+0.125	-0.040	+0.358	-0.042
2.4306 *	3.8519	0.5857	1.9626	2.596	1.4002	9.803	-2.434	+0.075	0	+0.281	+0.029
2.8082	4.8948	0.6877	2.2124	2.2043	1.5917	1.2668	-2.948	+0.050	-0.005	-0.107	+0.038
3.1059 *	5.4304	0.7348	2.3303	1.842	1.6786	1.4089	-2.992	-0.075	+0.010	-0.287	+0.034
3.7434 *	6.5206	0.8143	2.5535	1.5941	1.8407	1.6941	-2.528	-0.125	-0.010	-0.468	-0.017
4.0772 *	7.1017	0.8514	2.6649	1.408	1.9214	1.8439	-1.854	-0.075	-0.050	-0.532	-0.040
4.5358	8.0494	0.9038	2.8372	1.242	2.0313	2.0631	-0.660	+0.200	+0.020	+0.588	+0.032
Sum ... {								+0.800	+0.110	+1.524	+0.222
								-0.068	-0.020	-1.518	-0.223
$\epsilon_1$ .....								27	1	91.4	1
$\epsilon_2$ .....								1.7	1	3.3	1
$\epsilon_3$ .....								0.459	-0.020	7.101	-0.0316
Rel. error							219	0.36	3.91	1.6	

†  $y = 57.9167 \text{ mols.} - 0.38688 \text{ mols.}^2$   
‡  $y = 0.6201x - 0.09448x^2 + 0.001313x^3$ .

§  $y = 7.2859x - 1.96246x^2 + 0.45879x^3$ , and  
 $y = 2.8809 + 4.0857x - 0.86157x^2 + 0.01449x^3$ ,  $x = 1 \text{ mol.}$

## ADDENDUM.

A very important additional argument in favour of the real existence of changes of curvature has been obtained by ascertaining that a set of results, which can be represented perfectly by two parabolas showing a break, cannot be represented by a single parabola, even if this has as many constants in it as the two together had. The results with propyl alcohol in water (case I.) were taken for this investigation, and the calculations were simplified a little by representing the first half of them by a parabola with two instead of three constants (and the origin). The equation deduced for this parabola was  $y = .58662x + .01404x^2$ , and the values given by it were almost exactly identical with those given by the three-constant equations in Table II. column III., indeed the sum of the differences was  $.002^\circ$  less; so that the whole results may be represented by this equation together with that previously deduced for the second portion of the figure (the two containing together six constants and the origin) with a total apparent error .95 times the experimental error. A single equation with six constants and the origin was then deduced from the experimental results\*: the values obtained were

$$y = .554549x + .0643369x^2 - .02340953x^3 + .004282719x^4 \\ - .000320612037x^5 + .000008079213x^6;$$

and the differences between the values for  $y$  given by this equation and the experimental values were as follows:—

$p=2x.$	Diff.	$p=2x.$	Diff.
2 . . .	$-\overset{\circ}{.002}$	18 . . .	$-\overset{\circ}{.091}$
4 . . .	$+\overset{\circ}{.031}$	20 . . .	$-\overset{\circ}{.136}$
6 . . .	$-\overset{\circ}{.014}$	22 . . .	$-\overset{\circ}{.001}$
8 . . .	$-\overset{\circ}{.069}$	24 . . .	$+\overset{\circ}{.047}$
10 . . .	$+\overset{\circ}{.015}$	26 . . .	$+\overset{\circ}{.104}$
12 . . .	$-\overset{\circ}{.004}$	28 . . .	$-\overset{\circ}{.038}$
14 . . .	$+\overset{\circ}{.068}$	30 . . .	$-\overset{\circ}{.051}$
16 . . .	$+\overset{\circ}{.121}$	32 . . .	$+\overset{\circ}{.018}$

The sum of the errors is  $+.404^\circ$  and  $-.406^\circ$ , the mean,  $e_1$ , being  $.0506^\circ$ , or two and a half times greater than the experimental error; the  $e_2$  error is 10, and the  $e_3$  error is, as might

\* The deduction of this equation, in which long division and multiplication had to be employed, occupied ten days, although the values for  $y$  were the whole numbers from 1 to 16. This may give some conception of the desirability of obtaining some other method of examining results.

be anticipated, 1: thus the total error is  $\cdot 506^\circ$ , or 23.5 times greater than the experimental error, and 24.5 times greater than the total error of the two-curve drawing with the same number of constants, representing the existence of a break instead of continuity. This by itself would be an almost conclusive argument in favour of the real existence of this break.

I may take this opportunity of saying a few words in answer to the additional remarks which Prof. Rücker has published on the densities of Sulphuric Acid (*suprà*, p. 204).

(1) Prof. Rücker's statements as to my opinion respecting an equation of the form  $y = a + bx \dots gx^6$  may perhaps lead casual readers to the very erroneous conclusion that I used such an equation in my work on Sulphuric Acid, or that I regarded it as a probable expression of experimental results. The bent-lath curve may perhaps be mathematically even more complex than Prof. Rücker's curve (though I doubt whether Prof. Rücker can obtain such a simple definition of his curve as that which can be given of the bent-lath curve "the radius of curvature varies inversely as the distance from some fixed straight line"), but these curves which I used were, as was shown by the differentiation, practically very simple, being equivalent to the parabolas  $y = a + bx + cx^2$ . Prof. Rücker argues that if I subdivided the figures into these simple curves, I might have subdivided them still further into straight lines. I am certainly surprised that such an argument should be used by one who studied the question as closely as Prof. Rücker has done. The only legitimate representation of a series of results is evidently that which, *cæteris paribus*, represents fewest breaks; the parabola is just as probable a representation of physical properties as a straight line (perhaps more so), and as the curvilinear nature of the figure, in the present case, would evidently necessitate the use of more straight lines than of parabolas for drawings representing apparent errors of equal magnitude, the rectilinear representation is obviously unjustifiable.

(2) & (3) Prof. Rücker misunderstands me if he thinks that I advocated my representation as being superior to his as to the number of constants involved, or that I objected to his having obtained his equation by first making an approximation, and subsequently improving it. My objections to it were based solely on the grounds that it was an artificial and highly improbable representation of physical facts, and this, apparently, he does not refute.

(4) It is scarcely worth while to waste words in discussing

whether the modification introduced by Prof. Rücker's fourth term bears a sufficiently small proportion to the unmodified part to be correctly designated as a "hump" or not; but the illustration of converting a circle into an ellipse, which he quotes in justification of the excrescence which he placed on his approximate curve, appears to me to be a singularly unfortunate one, for the ellipse is *par excellence* the simplest and most natural modification of a circle, and, as such, continually presents itself in natural phenomena. Even if this were not the case, the alteration of one constant in an equation (from 1 to  $1-x^2$ ) is hardly comparable with the introduction of an entirely new arbitrary function with two arbitrary constants.

As Prof. Rücker so strenuously defends the legitimacy of his synthesizing his equation, I fail to see why he should object to my analyzing it back again into its original components, and thus obtaining suggestions of two of the breaks by the very means which was supposed to obliterate them: still less do I appreciate his clinching argument against the validity of these suggestions by showing that analysis in another direction is possible, which, while it fails in suggesting one of these two breaks, brings into prominence another one, the only one which I had thought his equation had really obliterated.

Nor do I see why because I informed Prof. Lodge, in 1889, that I had not then used empirical equations for detecting discontinuities, and did not place much faith in such a method, I should, now that a critic uses empirical equations against me, refrain from examining what evidence they afford for or against these discontinuities. I am merely meeting my opponent on his own ground by doing so.

(5) Prof. Rücker still considers that his equation was extended sufficiently far beyond the first and fourth of the breaks in question to justify him in saying that it bridged them over; if, however, instead of taking the average length of the sections of which the whole figure was composed, he had taken the actual lengths of those sections over which the ends of his curve projected, he would have found that the one end projected over rather less than  $\frac{2}{3}$  of the next section, the other over rather less than  $\frac{1}{3}$ ; distances which, I think, are very insufficient, especially as in the former case the sign of the difference between the observed and calculated values for the last included point is the same as that for the neighbouring points beyond it, to which his curve is evidently inapplicable, showing that the divergence has already begun before this last included point has been reached.

I scarcely think that Prof. Rücker is justified in stating that I have put forward anything which can legitimately be termed a "new solution" of these results—a one-break representation instead of a four-break one—or that "in the heat of argument" I have abandoned discontinuities on which I previously insisted. The simple fact is that I now find that a more complicated bent-lath curve or parabola will fit over the one particular break as to the existence of which I, from the first, expressed my doubts, but that even now I consider that there are objections against the use of such a curve, and, I may mention, I have found more objections since I stated this in my previous paper. It is true that, for the sake of comparison with Prof. Rücker's results, I extended the curves a short way beyond the two other breaks at the two ends, but this was effected, as I pointed out in the footnote on p. 141, only at the cost of increasing the apparent error to the extent of about one quarter as much again as that of my original drawing, and also of that of the experimental error.

The present state of the case may, I believe, be summarized as follows:—The chief argument in favour of the interpretation which I gave of my experiments was the concordance of the results obtained from various sources. Prof. Rücker's criticism starts by ignoring this argument, or, at any rate, does not attempt to explain how such a concordance was obtained, and deals only with a portion of one set of results. Prof. Rücker admits that these results show in places, either breaks, or something very like breaks, and he therefore confines his attention to a portion where all the changes are "minor" ones. He admits that the bridging over of these supposed breaks by a single equation does not necessarily disprove that they really are breaks, and all that he does is to construct such an equation, but an equation in favour of which as an expression of physical facts nothing can be urged. If the terms in this equation have no physical meaning then, I venture to think, it cannot be accepted as an expression of physical facts; whereas, if they have a physical meaning, then it is legitimate to analyze the equation, and by so doing we obtain, as I showed, additional proof, instead of disproof, of the very changes which I considered existed.

I quite agree with Prof. Rücker that further discussion, at any rate on these restricted lines, is useless. A mathematical investigation must be obviously confined to some special instances, and these instances must be worked up to a higher pitch of perfection than was possible in a work of which the

object was to prove a strong *prima facie* case by the accumulation of numerous instances from independent sources. I am at present engaged in obtaining results which, I trust, may be more suitable for mathematical criticism, and those mentioned in the foregoing paper may be taken as preliminary samples. I have also investigated a large number of instances in which the results are much less complicated than in the case of sulphuric acid, and I have thus accumulated a mass of evidence showing that changes similar to those already found do occur at simple molecular proportions. The accumulation of such evidence, however, is a work of time, but I hope in the end to succeed in dislodging Prof. Rücker from his present neutral position of neither affirming nor denying my conclusions.

February 1892.

LI. *On a Decisive Test-case disproving the Maxwell-Boltzmann Doctrine regarding Distribution of Kinetic Energy.* By LORD KELVIN\*.

THE doctrine referred to is that stated by Maxwell in his paper "On the Average Distribution of Energy in a System of Material Points" ('Camb. Phil. Soc. Trans.,' May 6, 1878, republished in vol. 2 of Maxwell's 'Scientific Papers') in the following words:—

"In the ultimate state of the system, the average kinetic energy of two given portions of the system must be in the ratio of the number of degrees of freedom of those portions."

Let the system consist of three bodies, A, B, C, all movable only in one straight line, K H L:

B being a simple vibrator controlled by a spring so stiff that when, at any time, it has very nearly the whole energy of the system, its extreme excursions on each side of its position of equilibrium are small:

C and A, equal masses:

C, unacted on by force except when it strikes L, a fixed barrier, and when it strikes or is struck by B:

A, unacted on by force except when it strikes or is struck by B, and when it is at less than a certain distance, H K, from a fixed repellent barrier, K, repelling with a force, F, varying according to any law, or constant, when A is between K and H, but becoming infinitely great when (if at any time) A reaches K, and goes infinitesimally beyond it.

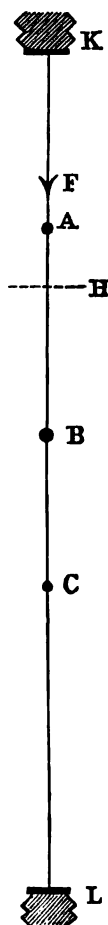
\* Communicated by the Author: from an advance-proof of the Proc. Roy. Soc. for April 28, 1892.



Suppose now A, B, C to be all moving to and fro. The collisions between B and the equal bodies A and C on its two sides must equalize, and keep equal, the average kinetic energy of A, immediately before and after these collisions, to the average kinetic energy of C. Hence, when the times of A being in the space between H and K are included in the average, the average of the *sum of the potential and kinetic energies* of A is equal to the average kinetic energy of C. But the potential energy of A at every point in the space H K is positive, because, according to our supposition, the velocity of A is diminished during every time of its motion from H towards K, and increased to the same value again during motion from K to H. Hence, the average kinetic energy of A is less than the average kinetic energy of C!

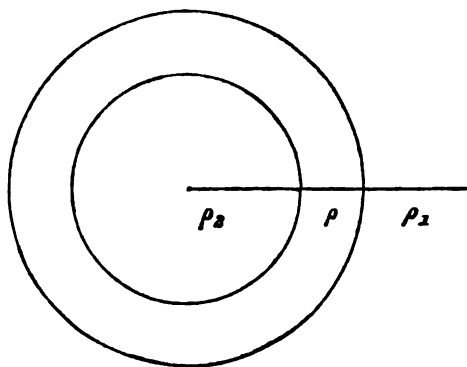
This is a test-case of a perfectly representative kind for the theory of temperature, and it effectually disposes of the assumption that the temperature of a solid or liquid is equal to its average kinetic energy per atom, which Maxwell pointed out as a consequence of the supposed theorem, and which, believed to be thus established, has been largely taught, and fallaciously used, as a fundamental proposition in thermodynamics.

It is in truth only for an approximately "perfect" gas, that is to say, an assemblage of molecules in which each molecule moves for comparatively long times in lines very approximately straight, and experiences changes of velocity and direction in comparatively very short times of collision, and it is only for the kinetic energy of the translatory motions of the molecules of the "perfect gas," that the temperature is equal to the average kinetic energy per molecule, as first assumed by Waterston, and afterwards by Joule, and first proved by Maxwell.



LII. *On the Theory of Surface Forces.*—III. *Effect of Slight Contaminations.* By LORD RAYLEIGH, *Sec.R.S.\**

**O**BSERVATION† having suggested that the lowering of surface-tension of water due to a film of oil falls off more rapidly when the film is attenuated than the thickness of the film itself can be supposed to do, I was led to examine the question theoretically; and the result shows that, according to the principles of Young and Laplace, the lowering of tension due to a very thin film should be in proportion, not to the thickness, but to the *square* of the thickness of the film. In the calculations which follow the fluids are supposed to be incompressible, a layer of density  $\rho$  and thickness  $\alpha$  being interposed between fluids of densities  $\rho_2$  and  $\rho_1$  (fig. 1). The



thickness  $\alpha$ , as well as the range of the forces, is supposed to be negligible in comparison with the radius of curvature  $R$  of the surfaces of separation.

By II. (16)‡ we have for the difference of pressures in the inner and outer liquids,

$$p_2 - p_1 = 2K(\rho_2^2 - \rho_1^2) - \int_{(1)}^{(2)} V d\rho$$

$$= 2K(\rho_2^2 - \rho_1^2) - (\rho - \rho_1) \cdot V(\rho, \rho_1) - (\rho_2 - \rho) \cdot V(\rho_2, \rho), \quad (1)$$

where  $V(\rho, \rho_1)$ ,  $V(\rho_2, \rho)$  denote the potentials at the surfaces of separation.

\* Communicated by the Author.

† See, for example, Miss Pockels on Surface Tension, 'Nature,' vol. xliii. p. 437 (1891).

‡ Phil. Mag. Feb. 1892.

Again, by II. (17),

$$\begin{aligned} V(\rho, \rho_1) &= \int_{-\infty}^{+\infty} 2\pi\rho'(1-\xi/R)\psi(\xi) d\xi \\ &= 2\pi(\rho_2 + \rho_1) \int_0^\infty \psi(\xi) d\xi - 2\pi(\rho_2 - \rho) \int_0^a \psi(\xi) d\xi \\ &\quad - \frac{2\pi}{R} \left\{ (\rho_2 - \rho_1) \int_0^\infty \psi(\xi) \xi d\xi - (\rho_2 - \rho) \int_0^a \psi(\xi) \xi d\xi \right\}, \end{aligned}$$

and

$$\begin{aligned} V(\rho_2, \rho) &= 2\pi(\rho_2 + \rho_1) \int_0^\infty \psi(\xi) d\xi + 2\pi(\rho - \rho_1) \int_0^a \psi(\xi) d\xi \\ &\quad - \frac{2\pi}{R} \left\{ (\rho_2 - \rho_1) \int_0^\infty \psi(\xi) \xi d\xi - (\rho - \rho_1) \int_0^a \psi(\xi) \xi d\xi \right\}. \end{aligned}$$

Consider now

$$(\rho - \rho_1) \cdot V(\rho, \rho_1) + (\rho_2 - \rho) \cdot V(\rho_2, \rho), \quad \dots \quad (2)$$

and collect separately the part independent of  $R$ , and that proportional to  $R^{-1}$ . For the first we have

$$2\pi(\rho_2^2 - \rho_1^2) \int_0^\infty \psi(\xi) d\xi, \quad \dots \quad (3)$$

the same as if  $\alpha=0$ .

For the second, omitting the factor  $-2\pi/R$ , we get

$$\begin{aligned} &(\rho - \rho_1) \left\{ (\rho_2 - \rho_1) \int_0^\infty \psi(\xi) \xi d\xi - (\rho_2 - \rho) \int_0^a \psi(\xi) \xi d\xi \right\} \\ &+ (\rho_2 - \rho) \left\{ (\rho_2 - \rho_1) \int_0^\infty \psi(\xi) \xi d\xi - (\rho - \rho_1) \int_0^a \psi(\xi) \xi d\xi \right\}, \end{aligned}$$

or

$$(\rho_2 - \rho_1)^2 \int_0^\infty \psi(\xi) \xi d\xi - 2(\rho - \rho_1)(\rho_2 - \rho) \int_0^a \psi(\xi) \xi d\xi. \quad \dots \quad (4)$$

Now

$$K = 2\pi \int_0^\infty \psi(\xi) d\xi,$$

so that

$$\rho_2 - \rho_1 = K(\rho_2^2 - \rho_1^2) + 2T/R, \quad \dots \quad (5)$$

where

$$\begin{aligned} T &= \pi(\rho_2 - \rho_1)^2 \int_0^\infty \psi(\xi) \xi d\xi \\ &\quad - 2\pi(\rho - \rho_1)(\rho_2 - \rho) \int_0^a \psi(\xi) \xi d\xi. \quad \dots \quad (6) \end{aligned}$$

The tension of the composite surface is thus given by (6).

If  $\alpha=0$ , we fall back upon the case of a simple sudden transition from  $\rho_2$  to  $\rho_1$ , and we get as before

$$T = \pi(\rho_2 - \rho_1)^2 \int_0^\infty \psi(\zeta) \zeta d\zeta. \quad (7)$$

Again, if  $\alpha = \infty$ ,

$$T = \pi \left\{ (\rho_2 - \rho)^2 + (\rho - \rho_1)^2 \right\} \int_0^\infty \psi(\zeta) \zeta d\zeta. \quad (8)$$

This corresponds to the formation of two independently acting tensions between the two pairs of liquids.

To pass from these verifications to circumstances of novelty, let us now suppose that  $\alpha$  is small compared with the range of the forces. When  $\zeta$  is small,  $\psi(\zeta)$  may be identified with  $\psi(0)$ , and we have

$$\delta T = -\pi(\rho - \rho_1)(\rho_2 - \rho) \cdot \psi(0) \cdot \alpha^2, \quad (9)$$

showing that in the limit  $\delta T$  is proportional to the *square* of the thickness  $\alpha$ .

According to Young's supposition I. (19)\* of a constant attraction within the range  $\alpha$ ,

$$\psi(\zeta) = \frac{1}{2}a(a^2 - \zeta^2) - \frac{1}{3}(a^3 - \zeta^3),$$

so that  $\psi(0) = \frac{1}{6}a^3$ ; and more generally whether  $\alpha$  be great or small,

$$\int_0^\alpha \psi(\zeta) \zeta d\zeta = \alpha^2 \left( \frac{1}{12}a^3 - \frac{1}{8}a\alpha^2 + \frac{1}{15}\alpha^3 \right). \quad (10)$$

The general formula (6) may be applied also to the case of a thin lamina by supposing that  $\rho_2 = \rho_1 = \rho_0$ . Thus

$$T = 2\pi(\rho - \rho_0)^2 \int_0^\alpha \psi(\zeta) \zeta d\zeta. \quad (11)$$

gives the tension of a lamina of density  $\rho$  and thickness  $\alpha$  surrounded by fluid of density  $\rho_0$ †. Here again, if  $\alpha$  be very small, the integral reduces to  $\frac{1}{6}\alpha^2\psi(0)$ , so that the tension varies as the square of  $\alpha$ .

It must be understood that the lamina is here supposed to be of uniform constitution, and that thus the result is probably inapplicable to soap-films.

\* Phil. Mag. Oct. 1890.

† In Maxwell's solution of this problem, Art. "Capillary Action," *Enc. Brit.*, the tension of the lamina is given at double the above value.

The law that the effect of a film when very thin is proportional to the square of the thickness is of considerable interest. It is here deduced upon the basis of Laplace's more special hypothesis that the specific differences between various bodies in relation to capillary properties may be represented by a simple coefficient in the expression for the law of force. But it is not difficult to see that the conclusion is really independent of this restriction, and that it holds good even though the law of force for every pair of bodies is entirely arbitrary.

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LIII. *Some Properties of Dried Hydrogen Sulphide Gas.*  
By R. E. HUGHES, B.Sc., F.C.S., *Jesus College, Oxford* \*.

IT was shown simultaneously by Thorpe that dry hydrogen sulphide mixed with carbon-disulphide vapour is without action on titanium sesquioxide (J. C. S. 1885, p. 492), and by Veley (*ibid.* p. 484) that the same gas when dry is without action on quicklime. In both cases the formation of a minute trace of water as a consequence of the reactions should cause them to proceed to their ultimate limit. A few months ago Mr. Veley suggested a similar investigation upon the conditions of reactions of hydrogen sulphide upon metallic oxides, other than those mentioned above.

Magnesia was selected as the first oxide, and the experiment was so arranged as to determine whether the weight of the oxide was in any respect altered by the passage of the hydrogen-sulphide gas over it.

By means of a T-tube connected up with a hydrogen-sulphide generator on the one limb, and a hydrogen generator on the other, a flow of either gas could be obtained at will, and at an easily regulated rate.

The gas first passed through a wash-bottle, which at the same time served to determine the rate of flow of the gas, which flow was such that on an average about 2 bubbles per second passed through.

The gas was dried by three U-tubes containing calcium chloride, and finally by a straight tube of pentoxide of phosphorus, containing at each end a loose plug of cotton-wool. The experimental vessel containing the oxide was a U-tube fitted with glass stoppers pierced, so that by simply revolving these stoppers the U-tube was sealed. The outgoing gas was then passed into a lime-tower; it was noticed that unless this lime was thoroughly slaked, the absorption of the gas was but

\* Communicated by Mr. V. H. Veley, M.A., University Museum, Oxford.

partial. The experimental tube was contained in a water-bath in which was placed a thermometer, so that the action at different temperatures might be investigated. It was noticed that where the dried hydrogen-sulphide gas came in contact with the filaments of cotton-wool covered with the pentoxide, a yellow deposit, presumably sulphur, was obtained. Whether this decomposing action is due to the finely divided oxide superficially covering the filaments, or not, is an open question. Moreover, it was observed that whilst the hydrogen-sulphide gas passed, the white oxide assumed a yellowish tint, which disappeared entirely when subsequently the hydrogen passed through.

The hydrogen was first passed through the apparatus for about one hour and a half to displace the air; the tube was then weighed, replaced in the water-bath, and the hydrogen sulphide passed through for about two hours, and the hydrogen sulphide again displaced by hydrogen before a second weighing was made. The temperature of the bath was read at intervals, and the mean of the readings taken as the temperature of investigation.

In an experiment conducted at a temperature of about  $15^{\circ}$ , the weight of magnesia taken was 0.7597 gram; after passing hydrogen sulphide, and again displacing this by hydrogen, the weight was found to be 0.7600 gram, or an increase of 0.0003 gram. Another experiment, conducted under precisely similar conditions, gave the following details. Weight of oxide taken was 0.6360 gram, which, after the passage of the gas, was found to weigh 0.6368 gram, showing an increase of 0.0008 gram; both of these increases are within the limits of errors of experiment and may safely be considered as such.

In an experiment conducted at a mean temperature of  $40^{\circ}$ , the result was of a similar character. Thus, having taken 0.8315 gram of the oxide, the increase in weight of this was 0.0011 gram. Hence it may be concluded that, under the conditions of these experiments, this change, which is an exothermic change, and therefore one which might be expected to take place, does *not* take place.

An experiment was made in which a drop of water from a pipette was dropped on to the magnesia, and the tube weighed. On passing the hydrogen sulphide through this mixture a rapid change is evident, the white oxide becoming of a greenish-yellow colour.

The temperature of the bath during this experiment was  $15^{\circ}$ . The weight of the oxide and water in the tube before

the experiment was 0.7235 gram; and after the gas had passed was 0.8435 gram, or an increase of 0.1200 gram.

Thus it is seen that the ratio of the increase when water is present with the magnesia is to the increase in weight in the absence of water as

$$\left. \begin{array}{l} 1200 : 3 \\ 1200 : 8 \\ 1200 : 11 \end{array} \right\} \begin{array}{l} \text{at a temperature of } 15^{\circ} \\ \text{at a temperature of } 15^{\circ} \\ \text{at } 40^{\circ}. \end{array}$$

The reason for the addition of liquid water to the oxide, instead of saturating the gas with moisture, is because Richardson has shown (J. C. S. li. p. 801) that in analogous reactions the water as steam has no influence on the chemical change.

Similar results were obtained with monoxide of barium, although the increases were slightly greater than in the case of magnesia. Thus in an experiment made at a temperature of  $15^{\circ}$  the weight of oxide of barium taken was 1.7465 gram, which, after the passage of the hydrogen-sulphide gas, showed an increase of 0.0034 gram.

Another experiment was conducted at a mean temperature of  $90^{\circ}$ . The weight of oxide taken was 3.3735 grams, which, after the passage of the gas and subsequent displacement by hydrogen, was found to weigh 3.3787 grams, or an increase of 0.0052 gram. Hence it appears from these experiments that dried hydrogen sulphide has no action on dried monoxide of barium between the temperatures of  $15^{\circ}$  and  $90^{\circ}$ .

With sesquioxide of iron the change that takes place is more evident than with any other oxide yet examined; although the results so far obtained point to the conclusion that with perfectly dry materials no change would take place\*. In one experiment 5.8108 grams of sesquioxide of iron showed an increase in weight, after the passage of the gas, of 0.0832 gram. The methods adopted for drying the oxide have not been sufficiently effectual to ensure complete absence of moisture, and the minute change that does take place is doubtless initiated by a trace of moisture already present†.

Experiments of a somewhat different character to the foregoing were then undertaken. Instead of determining the

\* The reaction between hydrogen sulphide and this substance presents the particular interest that it is of daily application in the purification of coal-gas. L. Wright [J. C. S. 1883, p. 156] in his experiments upon this point seems to have used the hydrated oxide only.

† Professor Odling tells me that although dried hydrogen sulphide does not act on the ordinary oxide of iron under the conditions of these experiments, yet an oxide of iron can be prepared which is acted upon by the gas: thus the compound  $\text{Fe}_2\text{O}_3\text{CaO}$ , got by fusing calc-spar and oxide of iron together, is such a body.

difference of weight as an indication of chemical change, the differences of colour produced by the formation of the sulphides of various metals, by the action of hydrogen sulphide on compounds of these metals, were taken. The method of experiment was as follows :—A short strip of ordinary filter-paper was taken and moistened with lead acetate, then dried in a water-bath and placed in a straight glass tube, which took the place of the experimental U-tube in the previously described experiments, and accordingly was connected up with the drying apparatus. Through this hydrogen was passed as before, then the hydrogen-sulphide gas for about two hours. The paper remained perfectly white and unaltered in the dry gas.

If, however, the paper was purposely only partially dried, or if a little liquid water was placed in contact with the dried paper, then the  $H_2S$  gas instantly turned the paper black\*. If two tubes, one containing the dried-lead-paper and the other a partially dried lead-paper, be placed side by side, and if the dried gas be passed first through the one tube and then through the other, the difference between the action of the gas on the paper in the two is very striking—the dried one remaining quite white throughout, whilst the other is instantly blackened by the gas.

A similar comparative experiment was performed in the case of paper moistened with a solution of arsenic tri-chloride : the dried paper remained quite unaltered, whilst the other was instantly turned yellow. With salts of tin, cadmium, bismuth, antimony, silver, copper, mercury, and cobalt, similar experiments were conducted, the results being in all cases exactly the same ; in the case of antimony, cadmium, and tin the differences are very striking. In all these cases, then, it was shown, by a comparative experiment of the kind described, that dried hydrogen sulphide has no action on the dried soluble salts of the metals before mentioned, whereas, if moisture be present and in contact with the substance investigated, the change at once takes place.

Further, it was observed that the dried gas has no action whatever on dry blue litmus-paper, whereas moist litmus-paper is instantly reddened.

The conclusion arrived at from these experiments is that dried hydrogen sulphide has no action on magnesia, baryta, sesquioxide of iron, or on salts of silver, copper, mercury, lead, bismuth, cadmium, arsenic, antimony, tin, and cobalt ; nor has it the power of reddening blue litmus-paper, whereas in

\* If, however, the lead-paper previously dried be moistened with absolute alcohol, instead of water, the darkening produced by hydrogen sulphide is very slight, although the gas is more soluble in alcohol than in water.



the presence of liquid water a chemical change does take place in all these cases.

Finally, it may be pointed out that the experiments of Mr. F. Wilson, of Keble College, and myself on the action of dried hydrochloric-acid gas on various carbonates, together with the experiments herein described, go to show that the compounds represented by the formula  $\text{HCl}$  and the formula  $\text{H}_2\text{S}$  are not (as is usually supposed) acids, but rather that they are acid anhydrides, not of the same order although of the same class as pentoxide of phosphorus or sulphuric anhydride. Just as in the case of many organic acids (for example, glycollic or lactic acids), we have more than one anhydride, so also in the case of the true sulphuric acid we may have the anhydride  $\text{SO}_3$  and the anhydride  $\text{H}_2\text{SO}_4$ . Perkin, from a study of the magnetic rotation of sulphuric and nitric acids, concludes that the formulæ  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  represent, not the acids, but anhydrides (J. C. S. 1887, p. 808, and 1889, p. 680). The pure compound  $\text{H}_2\text{SO}_4$ , as is well known, does not act on blue litmus\*, and probably is incapable of forming salts; and it seems probable, from the researches of Veley on nitric acid †, that this acid also, when in the pure state and free from nitrous acid, is likewise incapable of forming salts. So that the two criteria of true acids, namely, that they should be capable of turning blue litmus red, and also be capable of forming salts, fails in the cases of the molecules  $\text{HCl}$  ‡ and  $\text{H}_2\text{S}$ , and apparently also in the case of the molecules  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ .

In conclusion, I wish to express my indebtedness to Mr. V. H. Veley, M.A., for suggesting this investigation to me and for much valuable advice given during its progress.

University Laboratory, Oxford.

#### LIV. *Notices respecting New Books.*

*Index of Spectra. Appendix C. By W. MARSHALL WATTS, D.Sc., F.I.C., Senior Science Master in the Giggleswick Grammar School. Manchester: Abel Heywood & Son, 1892.*

THE present appendix to Dr. Watts's Index of Spectra contains some of the most important measurements recently made in connexion with spectroscopic work. By far the larger part of the book is occupied by the collected results of various observers on the spectrum of iron when volatilized in the electric arc. The numbers of Kayser and Runge, Rowland, Thalén, and Müller and Kempf

\* Marsh, 'Chem. News,' lxi. p. 2.

† Phil. Trans. 1891, p. 279.

‡ Julius Thomsen concludes from thermochemical considerations that the formula of the acid is  $\text{H}_3\text{ClO}$ . Possibly the true hydrosulphuric acid is  $\text{H}_4\text{SO}$ .

are all given, the table containing in all a record of about 4600 lines, extending from the region of the lithium (red) line to the extreme ultra-violet. After this follows a table of the air-lines of the solar spectrum, with their relative intensities when the sun is on the horizon and at medium altitude. The measurements from which this table was compiled are those of Becker, and the lines number about 1000. The volume is completed by a list of 14 lines in the spectrum of gadolinium chloride, the work of Lecoq de Boisbaudran, and 74 lines in the spectrum of a vacuum tube containing hydrogen, measured by Ames of the Johns Hopkins University. The latter measurements are rendered more interesting by their being compared with the values obtained from Balmer's formula, in which the oscillation frequency is taken as  $27418 \cdot 3 (1 - 4/m^2)$ , different values of  $m$  giving different lines. The agreement between the theoretical and actual frequencies is in many cases very remarkable.

JAMES L. HOWARD.

### *LV. Intelligence and Miscellaneous Articles.*

#### ON THE INFLUENCE OF PRESSURE ON THE VISCOSITY OF LIQUIDS.

BY R. COHEN.

THE results of a long experimental investigation on this subject are stated by the author as follows:—

I. The viscosity of water is diminished by pressure up to temperatures of  $40^\circ$ , as had already been found by Röntgen, Warburg, and Sachs.

II. No minimum of viscosity can be observed up to pressures of 900 atmospheres, and temperatures of  $25^\circ$ ; the change of viscosity is not proportional to the pressure, but increases more slowly.

III. In the case of water the viscosity changes greatly with the temperature, and in the interval of temperature from  $0$  to  $23^\circ$  it is greatest near  $0^\circ$ . It has not been decided whether the viscosity of water increases with pressure for temperatures above  $40^\circ$ .

IV. With concentrated aqueous solutions of NaCl and of  $\text{NH}_4\text{Cl}$  the viscosity of the solution increases with the pressure, and the percentage change is almost proportional to the pressure. The influence of temperature is small.

V. The more dilute a solution of NaCl is the more does the influence of the anomalous deportment of water preponderate, both as regards the influence of temperature, and also the influence of a further increase of pressure. From a 5-per-cent. to a 10-per-cent. solution there is for each concentration a definite temperature between  $2^\circ$  and  $22 \cdot 5$ , at which the influence of a pressure of 600 atmospheres on the viscosity is zero.

VI. In oil of turpentine the change of viscosity with the pressure is twenty times as great as with a saturated solution of NaCl, and is nearly proportional to the pressure. The direction of the change is the same. The influence of temperature is small, and is in the opposite direction to that of a solution of NaCl.—Wiedemann's *Annalen*, No. 4, 1892.

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## CONTENTS OF N<sup>o</sup> 204.—*Fifth Series.*

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XLVI. On the Resistances to Transverse Strain in Beams. By ROBERT CRADOCK NICHOLS .....	page 397
XLVII. Flexure of long Pillars under their own Weight. By MAURICE F. FITZGERALD .....	428
XLVIII. Note on the Change of Heat Conductivity on passing isothermally from Solid to Liquid. By C. BARUS .....	431
XLIX. Choking Coils. By Professor JOHN PERRY, D.Sc., F.R.S.	433
L. The Recognition of Changes of Curvature by Means of a Flexible Lath. By SPENCER UMFREVILLE PICKERING, F.R.S. ....	436
LI. On a Decisive Test-case disproving the Maxwell-Boltzmann Doctrine regarding Distribution of Kinetic Energy. By Lord KELVIN .....	466
LII. On the Theory of Surface Forces.—III. Effect of Slight Contaminations. By Lord RAYLEIGH, Sec. R.S. ....	468
LIII. Some Properties of Dried Hydrogen Sulphide Gas. By R. E. HUGHES, B.Sc., F.C.S., Jesus College, Oxford .....	471
LIV. Notices respecting New Books :—W. MARSHALL WATTS's Index of Spectra, Appendix C. ....	475
LV. Intelligence and Miscellaneous Articles :—	
On the Influence of Pressure on the Viscosity of Liquids, by R. Cohen .....	476

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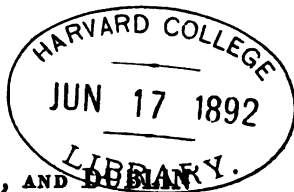
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LVI. *Quaternions as a practical Instrument of Physical Research.* By ALEXANDER M<sup>c</sup>AULAY, M.A., Ormond College, Melbourne\*.

IN writing the history of the Mathematics of the 19th century the historian will be brought face to face with a phenomenon hard to account for.

The inventor of quaternions was one of the greatest, perhaps the greatest, mathematician of this century. His work was varied and far reaching in its effects, but his name was always associated in the mind of the hearer with one well-defined group of his works—his quaternion researches. Thus the subject was brought forth in the full light of day, and has by no means passed into the limbo of forgotten things. Indeed the word "Quaternions" is fully as familiar even with non-mathematicians as the phrase "Cartesian Geometry."

But in spite of this he has left scarcely a successor. His two huge volumes form far more than half the whole original work that has been done in the subject. And this notwithstanding the fact that he deliberately did not attempt to apply the subject to Physics, although expressing his belief that in other hands it would prove a powerful instrument of research.

Can any cause be assigned for this extraordinary case of arrested development? The answer that by far the majority of physicists would give as to the physical aspect of the subject is, that the instrument is an admirable one for

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expressing the results obtained by the old-fashioned and artificial methods—but there their admiration would stop. The stern work, say they, of advancement into the unknown regions must be made by the clumsier but stronger means. When the country has been reduced to order and civilization, let quaternions be introduced as a luxury conducing to the recreation of the exhausted toilers. Nevertheless there is a small minority among these workers that venture to deny this slur on the character of their favourite implement. They assert that it has only to be used to be appreciated, and this to such an extent that all other geometrical implements are, or ought to be, cast aside in favour of it. I confess myself to be one of the extremest partizans of this sect. When directly I proceed, however, to state exactly what I believe to be the mission of quaternions in the domain of Physics, it will appear that in a short paper it is impossible to establish the contentions. The chief object of the present paper is to *shake* the belief of mathematical physicists. It is too much to hope to *overturn* that belief.

The first question to answer is the one already put—Can the apathy of physicists with regard to quaternions be accounted for if it be not that quaternions are unsuitable for their purposes? I confess that the more I think of this apathy the more extraordinary does it appear, and, as already hinted, it will probably prove an insoluble problem to the future historian of Mathematics. But reasons can be given, though not perfectly satisfactory—at least to my mind—for this almost criminal negligence.

Let us state the case against us. It can be put in very few words as follows—*Not much advance in Physics has been made by the aid of Quaternions.* I do not for a moment question this. It is too evident even for an advocate to blink. In all sincerity, however, I believe that this is all that can be assigned as reason for believing that quaternions do not provide means for extending the bounds of the known in the domain of Physics. Probably through the minds of more than one who listen to this is passing the thought—“But *I* have tried quaternions and *I* have found them wanting. I came to the subject unprejudiced, but I could produce nothing out of it.” Perhaps it is to the point to say that the present writer has passed through this phase. He, too, found that though quaternions were a fascinating study, they seemed to fail, for some inscrutable reason, to furnish the means for any real advance. Looking back, I think I can see the reason for this.

Maxwell, I fear, is responsible to a large extent for the



discredit into which quaternions have fallen among physicists. In his 'Electricity and Magnetism' (2nd edit. § 10) he remarks:—"I am convinced that the introduction of the ideas, *as distinguished from the operations and methods*, of Quaternions will be of great use to us in all parts of our subject." Now though very many study quaternions in a sort of dilettante way, very few who have not read and been struck with this passage do so before their mathematical ideas and methods are nearly or completely crystallized. Workers naturally find themselves, when still inexperienced in the use of quaternions, incapable of clearly thinking through them and of making them do the work of Cartesian Geometry, and they conclude that quaternions do not provide suitable treatment for what they have in hand. They then grow rather disgusted with these vexatious quaternions, and consoling themselves with the reflection that Maxwell, before penning the above extract, had had more experience than themselves, decide that the subject only requires a superficial study to be rendered of as great utility as it is capable.

The fact is that the subject requires a slight development before being applicable to many important physical questions, and these physicists do not continue their interest or enthusiasm for the subject sufficiently long to enable them to furnish that development.

Quaternions differ in an important respect from other branches of mathematics that are studied by mathematicians after they have in the course of years of hard labour laid the foundation of all their future work. In nearly all cases these branches are very properly so called. They each grow out of a definite spot of the main tree of mathematics, and derive their sustenance from the sap of the trunk as a whole. But not so with quaternions. To let these grow in the brain of a mathematician, he must start from the seed as with the rest of his mathematics regarded as a whole. He cannot graft them on his already flourishing tree, for they will die there. They are independent plants that require separate sowing and the consequent careful tending.

These are the explanations that can be given of the arrest in the development of quaternions that followed on the death of Hamilton.

It is now well to describe what I believe quaternions can do, and what should not be demanded of them in the researches of Physics. It is quite certain that the views about to be enunciated will be voted, to say the least, extreme, and it will not be possible to justify them in a short paper like the present. Still it seems proper to give them in all their nakedness.

I believe that Physics would advance with both more rapid and surer strides were quaternions introduced to serious study to the almost complete exclusion of Cartesian Geometry, except in an insignificant way, as a particular case of the former. All the geometrical processes occurring in physical theories and general physical problems are much simpler and more graceful in their quaternion than in their Cartesian garb. To illustrate the meaning here to be attached to "theory" and "general problem," take the case of elasticity. What is meant by the general theory of elasticity is well enough known. What I mean by a general problem is illustrated by St. Venant's torsion problem for *any* cylinder. The same problem for a cylinder of particular form would be called a *particular* problem. For such particular problems we require of course the theories specially constructed for the solution of particular problems, such as Fourier's theories, complex variables, spherical and ellipsoidal harmonics, &c. It will thus be seen that I do not propose to banish these theories, but merely Cartesian Geometry.

To establish these views it would be necessary to make good the following two statements:—

(1) *Quaternions are already in such a state of development as to justify the practically complete banishment of Cartesian Geometry from physical questions of a general nature.*

(2) *Quaternions will in Physics produce many new results that cannot be obtained by the rival and older geometrical method at all.*

To establish completely the first of these statements, it would be necessary to go over the whole ground covered by general physical questions. This would require a treatise of no small dimensions.

It is the second statement that must be considered of the greater importance. Unfortunately this, too, cannot be justified here. It has already been conceded that the subject requires a slight development, and this of course would necessitate a rather lengthy introduction. It is only after this development that I believe startling physical progress will be made by help of quaternions.

To bear out in part the assertions, however, a few examples of the application of quaternions to a variety of physical questions will be given. Some of the results below are of interest in themselves. They have not been chosen mainly on this account, however, but to illustrate as widely as is possible in a short paper the variety of the questions in which the subject may be expected to prove useful.

The following are the examples chosen:—(1) A theorem in

potentials illustrated by applying it to a general electrical problem. (2) Two examples in curvilinear coordinates. (3) A quaternion proof of a well-known theorem of Jacobi's of great utility in Physics. (4) A generalization of one of the well-known integrals of fluid motion. (5) The well-known particular solution of the differential equation expressing the conditions of equilibrium of an isotropic elastic solid subject to arbitrary bodily forces. (6) A short criticism of Prof. Poynting's theory of the transference of energy through an electric field.

In the proofs below, so far as quaternion knowledge is concerned, an acquaintance with Tait's 'Quaternions,' 3rd edit., only will be assumed. The following two equations from §§ 498, 499 of that treatise will be frequently required below.

$$\int d\rho q = \iint \nabla U \nu \nabla_1 q \, ds, \quad . . . . . (1)$$

$$\iint U \nu q \, ds = \iiint \nabla q \, ds. \quad . . . . . (2)$$

In equation (1)  $ds$  is an element of a surface,  $U\nu$  the unit normal at  $ds$ ,  $d\rho$  a vector element of the boundary, and  $q$  a quaternion function of a point in space. In equation (2)  $ds$  is an element of volume,  $ds$  an element of the bounding surface,  $U\nu$  the unit normal at  $ds$  pointing away from the region bounded. If the surface in (1) contain lines of discontinuity, or the volume in (2) surfaces of discontinuity in  $q$ , the equations are still true if such lines and surfaces of discontinuity are included in the boundary of the region. In such a case, of course, the elements  $d\rho$  and  $ds$  will each occur twice in the integrals (1) and (2) respectively, namely once for each of the two regions bounded by the element.

### I. Potentials.

In the volume and surface integrals that are now required it is necessary to pay attention to the following convention. Let  $\rho_a$  be the vector coordinate of a certain point under consideration, and let  $\rho_b$  be the vector coordinate of the element of volume  $ds$ . It will frequently happen that we have to deal with integrals of the form  $\iiint \phi(r) \, ds$ , where  $\phi$  is any quaternion function of a quaternion  $r$ . [In all the applications below,  $\phi$  will be a linear function, but this is not necessary.] *The form of  $\phi$  is a function of  $\rho_b$  only, and  $r$  is a function of  $\rho_b - \rho_a$  only.* Thus in the expression  $\nabla \iiint \phi(r) \, ds$  the only meaning that can be given to the differentiations implied by  $\nabla$  is such that these differentiations require  $\rho_a$  in

the vector  $\rho - \rho_a$  to vary. On the other hand, in the expression  $\iiint \nabla_1 \phi(r_1) ds$  (where the numerical suffixes imply, as throughout this paper they will imply, that the  $\nabla$  with a suffix only operates on the symbols which have the same suffix) either end of  $\rho_b - \rho_a$  might be considered the variable one. Since  $\phi$  will in general involve other  $\nabla$ 's which of necessity must presuppose  $\rho_b$  to be the variable, it is convenient to lay down the rule that for all  $\nabla$ 's under the integral sign  $\rho_b$  is supposed to be the variable. Thus when  $\nabla$  crosses the integral sign its sign must be changed, or

$$\nabla \iiint \phi(r) ds = - \iiint \nabla_1 \phi(r_1) ds. \quad . \quad . \quad (3)$$

With one exception the only value of  $r$  of equation (3) that will be required below is the scalar  $u$  defined by

$$u = T^{-1}(\rho_b - \rho_a). \quad . \quad . \quad . \quad (4)$$

It is well known that if  $q$  be any quaternion function of the position of a point,

$$4\pi q = \nabla^2 \iiint u q ds \quad . \quad . \quad . \quad (5)$$

or

$$4\pi q = - \nabla \iiint \nabla u q ds,$$

which gives by means of equation (2)

$$4\pi q = - \nabla \iiint u \nabla q ds + \nabla \iiint u \nabla q ds. \quad . \quad . \quad . \quad (6)$$

Here  $q$  may be discontinuous at specified surfaces.

This is the theorem in potentials spoken of. To show that it is really useful let us apply it to an electrical problem.

Maxwell's theory of the electromagnetic field is well enough known. Let us denote by the term "the ordinary theory" what is now to be described. In the ordinary theory there is a certain vector connected with an electromagnetic field, called the vector potential. This vector consists of two parts, one depending solely on the magnetism of the field and the other depending solely on the currents of the field. The vector magnetic force at a point also consists of two such parts. On the ordinary theory, the magnetic part of the vector potential  $\mathbf{A}$  and the magnetic part of the magnetic force  $\mathbf{H}$  are given in terms of the magnetic moment  $\mathbf{I}$  per volume by certain equations investigated in the 3rd Part (*Magnetism*) of Maxwell's 'Electricity and Magnetism.' *On the ordinary theory, the second part of each is obtained by assuming that each (closed) elementary current produces terms in  $\mathbf{A}$  and  $\mathbf{H}$  that would be produced by the corresponding magnetic shell.*

Maxwell makes no such assumptions as these, and does not show that they are on his theory true—as, indeed, he was not called upon to do. It is of interest, then, to inquire whether they are true on his theory. At a surface of discontinuity in any physical quantity let the two regions bounded be denoted by the suffixes  $a$  and  $b$ , and let us for brevity write  $[\ ]_{a+b}$  instead of  $[\ ]_a + [\ ]_b$ . Thus, for instance,  $U\nu_a$  will be a unit normal pointing away from the region  $a$ , *i. e.* into the region  $b$ , and  $[U\nu]_{a+b}=0$ , or  $U\nu_a = -U\nu_b$ . In place of the above assumptions Maxwell's theory gives

$$4\pi\mathbf{C} = \nabla\nabla\mathbf{H} . . . . . (7)$$

$$[\nabla U\nu\mathbf{H}]_{a+b}=0 . . . . . (8)$$

$$\nabla\nabla\mathbf{A} = \mathbf{B} = \mathbf{H} + 4\pi\mathbf{I} . . . . . (9)$$

$$[\mathbf{S}U\nu\mathbf{B}]_{a+b}=0 . . . . . (10)$$

It appears rather a formidable problem to deduce the ordinary theory from these equations, and to do it directly by Cartesianians would require rather a bewildering array of symbols.

Before proceeding to see what expressions the ordinary theory gives for  $\mathbf{A}$  and  $\mathbf{H}$  in terms of  $\mathbf{I}$  and  $\mathbf{C}$ , it is convenient to deduce from equation (10) the equation

$$[\nabla U\nu\mathbf{A}]_{a+b} = \nabla U\nu_a W, . . . . . (11)$$

where  $W$  is some scalar function of the position of a point. Equation (10) may be written

$$\mathbf{S}U\nu_a \mathbf{B}_{a-b} = 0, \text{ or } \mathbf{S}U\nu_a \nabla\mathbf{A}_{a-b} = 0.$$

$\therefore$  by equation (1) above  $\int \mathbf{S}d\rho_a \mathbf{A}_{a-b}$  is zero for any closed curve drawn on the surface.  $\therefore \int \mathbf{S}d\rho_a \mathbf{A}_{a-b}$  has the same value for any two reconcilable paths on the surface from one definite point to another; *i. e.* the resolved part of  $\mathbf{A}_{a-b}$  parallel to the surface is the resolved part of  $\nabla W$  parallel to the surface, where  $W$  is some scalar. Thus

$$U\nu_a \nabla U\nu_a \mathbf{A}_{a-b} = U\nu_a \nabla U\nu_a \nabla W.$$

Multiplying by  $U\nu_a$  we get equation (11).

The ordinary theory gives the following equations. Defining  $\mathbf{A}_0$  and  $\Omega$  by the equations

$$\mathbf{A}_0 = \iiint u \mathbf{C} ds, . . . . . (12)$$

$$\Omega = -\iiint \mathbf{S} \mathbf{I} \nabla u ds, . . . . . (13)$$

it will follow that

$$\mathbf{A} = \mathbf{A}_0 + \iiint \mathbf{V} \mathbf{I} \nabla u ds, . . . . . (14)$$

$$\mathbf{H} = -\nabla\Omega + \nabla\mathbf{A}_0; . . . . . (15)$$

i. e.  $\Omega$  is what is called the magnetic potential,  $\mathbf{A}_0$  is the part of the vector potential due to currents, and  $\nabla \mathbf{A}_0$  the part of the magnetic force due to the same cause. The statements that the parts of  $\mathbf{H}$  and  $\mathbf{A}$  due to magnetism are  $\nabla \iiint \mathbf{S} \mathbf{I} \nabla u ds$  and  $\iiint \mathbf{V} \mathbf{I} \nabla u ds$  respectively are taken directly from the third part of Maxwell's 'Electricity and Magnetism.' It remains to prove that the parts of  $\mathbf{H}$  and  $\mathbf{A}$  due to  $\mathbf{C}$  are  $\nabla \iiint u \mathbf{C} ds$  and  $\iiint u \mathbf{C} ds$  respectively. Since the \* part of  $\mathbf{H}$  due to magnetism is  $\nabla \iiint \mathbf{S} \mathbf{I} \nabla u ds$ , the part of  $\mathbf{H}$  contributed by a shell of strength  $c$  is

$$\begin{aligned} c \nabla \iiint \mathbf{S} \mathbf{U} \nabla u ds &= -c \iiint \mathbf{S} \mathbf{U} \nabla \cdot \nabla u ds = c \iiint \mathbf{V} \mathbf{U} \nabla \cdot \nabla u ds [\because \nabla^2 u = 0] \\ &= -c \iiint \nabla \mathbf{V} \mathbf{U} \nabla u = c \nabla \iiint \mathbf{V} \mathbf{U} \nabla u ds = c \nabla \int u d\rho [\text{equation (1) above}]. \end{aligned}$$

Hence the part of  $\mathbf{H}$  contributed by  $\mathbf{C}$  is  $\nabla \iiint u \mathbf{C} ds$ . This proves equation (15).

Since the part contributed to  $\mathbf{A}$  by  $\mathbf{I}$  is  $\iiint \mathbf{V} \mathbf{I} \nabla u ds$ , the part contributed by the shell is  $c \iiint \mathbf{V} \mathbf{U} \nabla u ds = c \int u d\rho$ . Hence the part contributed by  $\mathbf{C}$  is  $\iiint u \mathbf{C} ds$ . This proves equation (14).

It remains to see how far Maxwell's theory agrees with equations (12) to (15). Since  $\mathbf{S} \nabla (\mathbf{V} \nabla \mathbf{A}) = 0$ , we have from equation (9)  $\mathbf{S} \nabla \mathbf{H} = -4\pi \mathbf{S} \nabla \mathbf{I}$ . Hence from equation (7)

$$\nabla \mathbf{H} = 4\pi (\mathbf{C} - \mathbf{S} \nabla \mathbf{I}).$$

Again, from equation (10),  $[\mathbf{S} \mathbf{U} \nabla \mathbf{H}]_{a+b} = -4\pi [\mathbf{S} \mathbf{U} \nabla \mathbf{I}]_{a+b}$ . Hence from equation (8),

$$[\mathbf{U} \nabla \mathbf{H}]_{a+b} = -4\pi [\mathbf{S} \mathbf{U} \nabla \mathbf{I}]_{a+b}.$$

Putting then in equation (6)  $q = \mathbf{H}$ ,

$$\begin{aligned} \mathbf{H} &= \nabla \iiint u \mathbf{S} \mathbf{U} \nabla \mathbf{I} ds + \nabla \iiint u (\mathbf{C} - \mathbf{S} \nabla \mathbf{I}) ds \\ &= \nabla \iiint (u \mathbf{C} + \mathbf{S} \mathbf{I} \nabla u) ds \end{aligned}$$

by equation (2). This is equation (15).

Again, substituting  $\mathbf{A}$  for  $q$ , and utilizing equations (9), (11),

$$\begin{aligned} 4\pi \mathbf{A} &= \nabla \iiint u (\mathbf{H} + 4\pi \mathbf{I}) ds - \nabla \iiint u \mathbf{V} \mathbf{U} \nabla \mathbf{W} ds \\ &\quad + \nabla (-\iiint u \mathbf{S} \mathbf{U} \nabla \mathbf{A} ds + \iiint u \mathbf{S} \nabla \mathbf{A} ds). \end{aligned}$$

\* In what follows I deliberately give in their quaternion form certain results that might be quoted from Maxwell's 'Electricity and Magnetism,' in order to show that the problem when thus worked out at full is by no means a long one when treated by means of quaternions.

Here, as usual, the element  $ds$  is taken twice, viz., once for each region bounded, except in the expression

$$-\nabla \iint u \nabla U \nu_a \nabla W ds,$$

where it is taken only once.

This last expression requires transformation. If the surface of discontinuity in  $\mathbf{B}$  or  $\nabla \nabla \mathbf{A}$  is not closed, we see by equation (11) that the component of  $\nabla W$  parallel to the surface is zero at the edges; i. e.,  $W$  is constant at the edges. Let  $W_0$  be this constant value. In this case

$$\begin{aligned} -\nabla \iint u \nabla U \nu_a \nabla W ds &= -\nabla \iint u \nabla U \nu_a \nabla (W - W_0) ds \\ &= \nabla \left\{ \iint (W - W_0) \nabla U \nu_a \nabla u ds - \int u (W - W_0) d\rho \right\} [\text{equation (1)}]. \end{aligned}$$

The line integral is zero  $\because W = W_0$  at the edges. The surface integral gives

$$\begin{aligned} -\iint (W - W_0) \nabla_1 \nabla U \nu_a \nabla_1 u_1 ds &= \iint (W - W_0) \nabla U \nu_a \nabla \cdot \nabla u ds \\ &= -\iint (W - W_0) S U \nu_a \nabla \cdot \nabla u ds [\because \nabla^2 u = 0] = \nabla \iint (W - W_0) S U \nu_a \nabla u ds. \end{aligned}$$

If the surface is a closed one we may regard any point on it as the bounding curve, or we may proceed thus:—

$$\begin{aligned} -\iint u \nabla U \nu_a \nabla W ds &= -\iiint \nabla \nabla (u \nabla W) d\tau [\text{equation (2)}] \\ &= -\iiint \nabla \nabla u \nabla W d\tau = \iiint \nabla \nabla (W \nabla u) d\tau = \iint W \nabla U \nu_a \nabla u ds. \end{aligned}$$

Hence

$$-\nabla \iint u \nabla U \nu_a \nabla W ds = \nabla \iint W \nabla U \nu_a \nabla u ds = \nabla \iint W S U \nu_a \nabla u ds$$

by the same transformation as for

$$\nabla \iint (W - W_0) \nabla U \nu_a \nabla u ds.$$

Defining then the scalar  $w$  by the equation

$$4\pi w = \iint (W - W_0) S U \nu_a \nabla u ds - \iint u S U \nu_a \nabla W ds + \iiint u S \nabla \nabla \mathbf{A} d\tau,$$

we have

$$4\pi(\mathbf{A} - \nabla w) = 4\pi \iiint \nabla \mathbf{I} \nabla u ds + \iiint \nabla \mathbf{H} \nabla u ds$$

and

$$\begin{aligned} \iiint \nabla \mathbf{H} \nabla u ds &= \iiint u \nabla \nabla \mathbf{H} d\tau + \iint u \nabla \mathbf{H} U \nu_a ds [\text{equation (2)}] \\ &= 4\pi \iiint u \mathbf{C} d\tau [\text{equations (7), (8)}]. \end{aligned}$$

Hence

$$\mathbf{A} = \mathbf{A}_0 + \iiint \nabla \mathbf{I} \nabla u ds + \nabla w, \quad . \quad . \quad . \quad (16)$$

so that Maxwell's theory differs from the ordinary theory solely by having an arbitrary vector of the form  $\nabla w$  in  $\mathbf{A}$ .

II. *Curvilinear Coordinates.*

Let  $\phi$  be the stress-function, so that the equation of motion of an elastic solid is

$$\phi\Delta + D\mathbf{F} = D\ddot{\epsilon}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where  $D$  is the density,  $\mathbf{F}$  is the external force per unit mass,  $\epsilon$  is the (small) displacement of a point, and  $\phi\Delta$  is defined by the equation

$$\phi\Delta \equiv \frac{d\phi i}{dx} + \frac{d\phi j}{dy} + \frac{d\phi k}{dz}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Required to deduce from equation (17) Lamé's transformation into curvilinear coordinates. Changing the  $\rho, S, T, U, \partial/\partial s_1, \partial/\partial s_2, \partial/\partial s_3$ , of equations (43), § 237 of Ibbetson's 'Elasticity,' into  $D, L, M, N, D_\xi, D_\eta, D_\zeta$  respectively, those equations become

$$\begin{aligned} D_\xi P + D_\eta N + D_\zeta M + D(\Xi - \ddot{u}) \\ = (P - Q)_\xi \varpi_\zeta + (P - R)_\xi \varpi_\eta + N(2 \cdot \eta \varpi_\zeta + \eta \varpi_\xi) + M(2 \cdot \zeta \varpi_\eta + \zeta \varpi_\xi) \end{aligned} \quad (19)$$

and two similar equations. The notation is as follows:—

$$\xi = \text{constant}, \quad \eta = \text{constant}, \quad \zeta = \text{constant}, \quad . \quad . \quad (20)$$

are three families of surfaces cutting everywhere orthogonally.  $\xi \varpi_\eta, \xi \varpi_\zeta$ \* are defined as the curvatures of the normal sections of the  $\xi$  surface through the tangents to the  $\xi\eta$  and  $\xi\zeta$  curves respectively. If  $I, J, K$  be unit vectors normal to the three surfaces  $\xi, \eta, \zeta$  respectively, then  $P, Q, R, L, M, N, \Xi, H, Z, u, v, w$ , are defined by the equations

$$\phi I = PI + NJ + MK, \quad \&c., \quad \&c. \quad . \quad . \quad . \quad (21)$$

$$\mathbf{F} = \Xi I + HJ + ZK \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$\epsilon = uI + vJ + wK. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Lastly,  $D_\xi, D_\eta, D_\zeta$  denote, not differentiations with regard to  $\xi, \eta, \zeta$ , but differentiations *per unit length* in the directions of  $I, J, K$  respectively. So much for the rather formidable

\* It will be noticed that while giving the same definition as Ibbetson ('Elasticity,' § 232) of  $\xi \varpi_\eta, \xi \varpi_\zeta$  equation (19) is not the same with reference to these symbols as his equation (43) § 237. This is because his definition is inconsistent with the meanings he assigns to the symbols. To obtain those meanings he ought to give the inconvenient definition that  $\xi \varpi_\eta, \xi \varpi_\zeta$  are the curvatures of the normal sections of  $\xi$  through the tangents to  $\xi\zeta, \xi\eta$  respectively. This is simply illustrated by equation (66) § 243, where with  $\theta$  for colatitude and  $\omega$  for longitude he asserts that  $\varpi_\omega = -\cot \theta/r$ , whereas with his definitions, which I adopt, this should clearly be  $\varpi_r = -\cot \theta/r$ .



notation. Now compare the following proof with the Cartesian one given in Ibbetson's 'Elasticity,' § 237. We have

$$\nabla = ID_{\xi} + JD_{\eta} + KD_{\zeta} \quad \dots \quad (24)$$

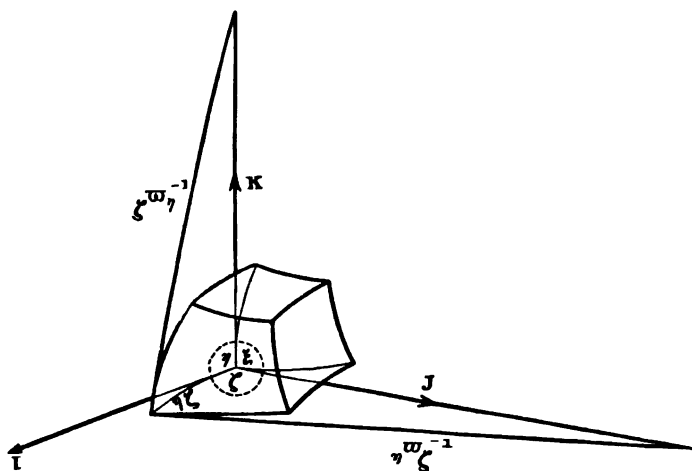
Hence

$$\phi\Delta = \Sigma D_{\xi}\phi \cdot I = \Sigma \{D_{\xi}(\phi I) - \phi D_{\xi}I\},$$

or in full

$$\begin{aligned} \phi\Delta = & D_{\xi}(PI + NJ + MK) + D_{\eta}(NI + QJ + LK) \\ & + D_{\zeta}(MI + LJ + RK) - \phi(D_{\xi}I + D_{\eta}J + D_{\zeta}K) \quad \dots \quad (25) \end{aligned}$$

Since the curve  $\eta\zeta$  is a principal line of curvature on each of



the surfaces  $\eta$  and  $\zeta$  (Dupin's theorem) it is obvious (see figure) that if a point move with unit velocity along it, carrying the system  $I, J, K$  of vectors, this system will be rotating with (vector) angular velocity

$$-J_{\zeta}\omega_{\eta} + K_{\eta}\omega_{\zeta}.$$

Hence

$$D_{\xi}I = \eta\omega_{\zeta}J + \zeta\omega_{\eta}K, \quad D_{\xi}J = -\eta\omega_{\zeta}I, \quad D_{\xi}K = -\zeta\omega_{\eta}I. \quad (26)$$

$\therefore D_{\xi}I + D_{\eta}J + D_{\zeta}K = I(\xi\omega_{\eta} + \xi\omega_{\zeta}) + J(\eta\omega_{\zeta} + \eta\omega_{\xi}) + K(\zeta\omega_{\xi} + \zeta\omega_{\eta});$   
and therefore

$$\begin{aligned} & \phi(D_{\xi}I + D_{\eta}J + D_{\zeta}K) \\ & = I\{P(\xi\omega_{\eta} + \xi\omega_{\zeta}) + N(\eta\omega_{\zeta} + \eta\omega_{\xi}) + M(\zeta\omega_{\xi} + \zeta\omega_{\eta})\} + J\{\} + K\{\}. \quad (27) \end{aligned}$$

Hence

$$\begin{aligned} \phi\Delta = & I\{(D_{\xi} - \xi\omega_{\eta} - \xi\omega_{\zeta})P + (D_{\eta} - \eta\omega_{\zeta} - \eta\omega_{\xi})N + (D_{\zeta} - \zeta\omega_{\xi} - \zeta\omega_{\eta})M\} \\ & + I\{-\eta\omega_{\zeta}N - \zeta\omega_{\eta}M + \xi\omega_{\zeta}Q + \xi\omega_{\eta}R\} + J\{\} + K\{\}; \end{aligned}$$

or

$$\phi\Delta = I\{(D_\xi P + D_\eta N + D_\zeta M) - (P-Q)\xi\varpi_\zeta - (P-R)\xi\varpi_\eta - N(2_\eta\varpi_\zeta + \eta\varpi_\xi) - M(2_\zeta\varpi_\eta + \zeta\varpi_\xi)\} + J\{\} + K\{\}. \quad (28)$$

Substituting this value of  $\phi\Delta$  and the values of  $F$  and  $\epsilon$  given by equations (22) and (23) in equation (17) we get equation (19).

As a second example in curvilinears let us find the strain in this notation. Let  $\psi$  be the pure strain due to  $\epsilon$ , i.e. let

$$2\psi\omega = -S\omega\nabla.\epsilon - \nabla_1 S\omega\epsilon_1 \dots \dots \dots (29)$$

With the usual notation ( $e, f, g, a, b, c$ ) for the coordinates of pure strain, we have

$$2\psi I = 2eI + cJ + bK, \&c., \&c. \dots \dots \dots (30)$$

Substituting in equation (29) for  $\nabla$  from equation (24), we get

$$2\psi I = D_\xi\epsilon - ISID_\xi\epsilon - JSID_\eta\epsilon - KSID_\zeta\epsilon.$$

But [equation (23)]

$$D_\xi\epsilon = ID_\xi u + JD_\xi v + KD_\xi w + uD_\xi I + vD_\xi J + wD_\xi K \\ = I(D_\xi u - \eta\varpi_\zeta v - \zeta\varpi_\eta w) + J(D_\xi v + \eta\varpi_\zeta u) + K(D_\xi w + \zeta\varpi_\eta u) \quad [\text{eq. (26)}]$$

Similarly,

$$-SID_\eta\epsilon = D_\eta u + \xi\varpi_\zeta v, \quad -SID_\zeta\epsilon = D_\zeta u + \xi\varpi_\eta w.$$

Hence

$$2\psi I = I(2D_\xi u - \eta\varpi_\zeta v - \zeta\varpi_\eta w) + J\{(D_\xi + \xi\varpi_\zeta)v + (D_\eta + \eta\varpi_\zeta)u\} \\ + K\{(D_\xi + \xi\varpi_\eta)u + (D_\zeta + \zeta\varpi_\eta)w\},$$

whence from equation (30)

$$2e = 2D_\xi u - \eta\varpi_\zeta v - \zeta\varpi_\eta w, \quad 2f = \dots, \quad 2g = \dots \dots \dots (31)$$

$$2a = (D_\eta + \eta\varpi_\xi)w + (D_\zeta + \zeta\varpi_\xi)v, \quad 2b = \dots, \quad 2c = \dots$$

Compare this with § 234 of Ibbetson's 'Elasticity.'

### III. Jacobi's Theorem.

... of the Calculus of Variations' ... enunciated. ... of  $x, y, z$ , and  $G$  any function of ... Let  $x, y, z$  be three functions ...  $\partial z$ . ...  $\lambda, \mu, \nu$ . When expressed in ...  $\phi$ ; and when expressed ...  $\partial\phi/\partial\lambda, \partial\phi/\partial\mu, \partial\phi/\partial\nu$ , let  $G$  be de-

$$= \frac{\partial(x, y, z)}{\partial(\lambda, \mu, \nu)}.$$

Then shall

$$\begin{aligned} & \Pi \left\{ \frac{\partial G}{\partial} - \frac{\partial}{\partial x} \left( \frac{\partial G}{\partial \frac{\partial v}{\partial x}} \right) - \frac{\partial}{\partial y} \left( \frac{\partial G}{\partial \frac{\partial v}{\partial y}} \right) - \frac{\partial}{\partial z} \left( \frac{\partial G}{\partial \frac{\partial v}{\partial z}} \right) \right\} \\ &= \Pi \frac{\partial \Gamma}{\partial \phi} - \frac{\partial}{\partial \lambda} \left( \frac{\partial (\Pi \Gamma)}{\partial \frac{\partial \phi}{\partial \lambda}} \right) - \frac{\partial}{\partial \mu} \left( \frac{\partial (\Pi \Gamma)}{\partial \frac{\partial \phi}{\partial \mu}} \right) - \frac{\partial}{\partial \nu} \left( \frac{\partial (\Pi \Gamma)}{\partial \frac{\partial \phi}{\partial \nu}} \right) \end{aligned}$$

We may omit the first term on each side since it is easy to see that  $\partial G / \partial v = \partial \Gamma / \partial \phi$ .

Expressed in quaternion language this may be put thus:—

Let  $v$  be any scalar function of  $\rho$  a vector, and  $G$  any scalar function of  $\rho$ ,  $v$ , and  $\nabla v$ . Let  $\rho$  be a function of  $\rho'$ . When expressed in terms of  $\rho'$ , let  $v$  be denoted by  $v'$ ; and when expressed in terms of  $\rho'$ ,  $v'$ , and  $\nabla' v'$  [ $\nabla'$  standing towards  $\rho'$  as  $\nabla$  towards  $\rho$ ], let  $G$  be denoted by  $G'$ . Lastly, let

$$m = \frac{S d \rho_a' d \rho_b' d \rho_c'}{S d \rho_a d \rho_b d \rho_c},$$

where  $d \rho_a, d \rho_b, d \rho_c$  are three arbitrary increments of  $\rho$  and  $d \rho_a', d \rho_b', d \rho_c'$  the consequent increments in  $\rho'$ . Then shall

$$m^{-1} S \nabla \nabla_v G = S \nabla' \nabla_{v'} (m^{-1} G'),$$

where  $v, v'$  stand for  $\nabla v, \nabla' v'$ , and  $\nabla_v, \nabla_{v'}$  stand towards  $v, v'$  as  $\nabla, \nabla'$  towards  $\rho, \rho'$ .

We have

$$d \rho' = -S d \rho \nabla_1 \rho' = \chi d \rho$$

say. Also

$$S d \rho \nabla v = S d \rho' \nabla' v' = S d \rho \chi' \nabla' v',$$

where as usual  $\chi'$  stands for the conjugate of  $\chi$ . Hence

$$v = \chi' v',$$

or generally

$$\nabla_1 = \chi' \nabla_1'.$$

Again,

$$S d v' \nabla_{v'}' G' = S d v \nabla_v G = S d v \chi \nabla_v G.$$

Hence

$$\nabla_{v'}' G' = \chi \nabla_v G.$$

Hence

$$S \nabla \nabla_v G = S \chi' \nabla_1' \chi_1^{-1} \nabla_{v_1}' G_1'$$

$$S \Delta' \chi \chi^{-1} \nabla_{v_1}' G_1' + S \chi_1'^{-1} \chi' \nabla_1' \nabla_{v'}' G'$$

$$= S \nabla' \nabla_{v'}' G' + S \chi_1'^{-1} \chi' \nabla_1' \nabla_{v'}' G'.$$

Now

$$\chi_1'^{-1}\chi'\nabla_1' = -\chi'^{-1}\chi_1'\nabla_1' [\because \chi_1'^{-1}\chi_1'\nabla_1' = \nabla 1 = 0];$$

and, as will be proved directly,  $m_1^{-1}\chi_1'\nabla_1' = 0$ , so that

$$\chi_1'\nabla_1' = -m\chi'\nabla'(m^{-1}).$$

Hence

$$m^{-1}S\nabla\nabla_s G = m^{-1}S\nabla'\nabla_s'G' + S\nabla'(m^{-1})\nabla_s'G' = S\nabla'\nabla_s'(m^{-1}G').$$

This theorem is a particular case of one of several allied quaternion theorems that I have found very useful in Physics, but which have not yet been published. The proof just given is not the simplest or most natural quaternion proof, but is the simplest I can furnish when the theorem is divorced from what may be called its natural surroundings.

It still remains to prove that  $m_1^{-1}\chi_1'\nabla_1' = 0$ . If it were assumed, which is true, and which ought to be thoroughly familiar to every mathematical physicist, that

$$2m^{-1}\chi'\omega = -\nabla\rho_1\rho_2S\omega\nabla_1'\nabla_2',$$

the statement would be obvious. As unhappily, however, this is not generally known, the following indirect method of proof may be adopted. Take  $\rho$  and  $\rho'$  as the coordinate vectors of any point in two different positions. Then

$$0 = \iint Uvds = \iint m^{-1}\chi'Uv'ds' = \iiint m_1^{-1}\chi_1'\nabla_1'ds' [\text{equation (2)}].$$

This being true for any space, is true for a single element  $ds'$ , and therefore  $m_1^{-1}\chi_1'\nabla_1' = 0$ . The assumption that

$$Uvds = m^{-1}\chi'Uv'ds'$$

is easily seen to follow from the definition of  $m$ . For  $Uvds$  may be taken as  $Vdp_\rho d\rho_\rho$  and  $Uv'ds'$  as  $Vdp_\rho'd\rho_\rho'$ , so that the definition of  $m$  gives

$$Sdp_\rho Uvds = m^{-1}Sdp_\rho'Uv'ds' = m^{-1}Sdp_\rho\chi'Uv'ds'.$$

#### IV. *An Integral of the Equations of Fluid Motion.*

The integral I am about to give I do not propose to prove, because what seems to me the best quaternion proof requires properties of quaternions not proved in Tait's 'Quaternions.' It has been said over and over again that quaternions in Physics are only useful for expressing the results obtained by other processes, and, perhaps, occasionally for furnishing a neater proof of a truth when it has been discovered by other means. To persons holding such views, of course there can be no difficulty in furnishing a Cartesian proof of a quaternion theorem. I will enter very fully into detail in the statement of the theorem, to leave no doubt as to the meaning.

Let  $p$  be the pressure,  $\sigma$  the (vector) velocity, and  $v$  the force potential at any point of a fluid. Let  $\int dp/(\text{density})$  be put as usual  $= P$ . Let  $d/dt$  denote differentiation with regard to time *which follows the motion of matter*. The fluid may be finite or infinite, and there may be any possible kind of discontinuity in the motion.  $\iint_s$  denotes a surface integral taken over the true boundary of the fluid (including the surface at infinity if the fluid is infinite).  $\iiint$  denotes a surface integral taken over this true boundary, and also over both sides of any surface of discontinuity, which is thus supposed to bound the region on both sides. The surface to which  $\iint_s$  refers may not always contain the same fluid particles, since for instance fissures may form leading to new parts of the true boundary, or such fissures may close up. When a fissure is in process of formation  $\iint_s$  refers to the boundary thus created from the instant when the portions of fluid begin to move asunder. Let  $\tau$  be twice the (vector) spin; i. e.  $\tau = \nabla \nabla \sigma$ . Let  $n$  be the convergence; i. e.  $n = S \nabla \sigma$ . Let  $N$  be\* the surface expansion; i. e.  $N = -S U \nu \sigma$ . Let  $u$  be defined by equation (4) above. Then

$$4\pi(v+P) = \iint_s (v+P) S U \nu \nabla u ds - \left\{ \iint_s u \frac{d(N ds)}{dt} + \iiint u \frac{d(n ds)}{dt} \right\} - \iiint S \{ V \sigma \tau - n \sigma + \nabla(\sigma^2/2) \} \nabla u ds. \quad (32)$$

This may be put also in the form

$$4\pi(v+P-\sigma^2/2) = \iint_s (v+P) S U \nu \nabla u ds - \iint (\sigma^2/2) S U \nu \nabla u ds - \left\{ \iint_s u \frac{d(N ds)}{dt} + \iiint \frac{d(n ds)}{dt} \right\} - \iiint S (V \sigma \tau - n \sigma) \nabla u ds. \quad (33)$$

The usual integral for an infinite irrotational continuously moving fluid,

$$v+P-\sigma^2/2+\partial\phi/\partial t=H,$$

can easily be shown to be a particular case. It may be noticed that

$$V \sigma \tau - n \sigma = -V \nabla \sigma \sigma,$$

and therefore

$$-S \nabla u (V \sigma \tau - n \sigma) = S \nabla u \nabla \sigma \sigma.$$

\* It might be thought that in analogy to  $n$  it would be better to put  $N = S U \nu \sigma$ , but by considering the analogy between ordinary convergence and a contracting bubble it will be seen that the definition of  $N$  given is perhaps better. It must be remembered that  $U \nu$  points from the fluid bounded and therefore into the bubble.

I sought and found the integral in attempting to consider, from a fresh point of view, Sir William Thomson's vortex-atom theory and Prof. Hicks's proposed modification of it; and though I have not made any serious attempt to apply it in this direction, I still think that it can be made of use in discussing how large groups of vortices act on other large groups.

There would be apparent attractions or repulsions of a definite kind between vortices if the acceleration  $d\sigma/dt$  could be expressed as a function of the vortices. In both the theories just mentioned the fluid is assumed to be incompressible and subject to no external forces, so that  $v=0$ . In Sir William Thomson's theory the fluid is unbounded, and in Prof. Hicks's it is infinite but bounded at certain places by what may be called bubbles. In these bubbles the pressure is zero. We have then from equation (32) for both cases

$$4\pi\dot{\sigma} = \nabla \left\{ \iint u \frac{d(Nds)}{dt} + \iiint S \{ \nabla\sigma\tau - \nabla(\sigma^2/2) \} \nabla u ds \right\}; \quad (34)$$

so that the vortices will move as though subject to a force potential  $w$  given by

$$4\pi w = - \iint u \frac{d(Nds)}{dt} - \iiint S \{ \nabla\sigma\tau - \nabla(\sigma^2/2) \} \nabla u ds. \quad (35)$$

I do not propose to discuss the bearing of these results here. I merely give them to indicate that the integral just given may, notwithstanding its apparent complexity when stated perfectly generally, prove of great utility.

A very different form may be given to the above integral. It will probably hint to one familiar with quaternion methods one way of proving the result. It is convenient to change the notation. Instead of the former  $\sigma$ ,  $U\nu$ ,  $ds$ ,  $d\varsigma$ , and  $\nabla$ , write now  $\sigma'$ ,  $U\nu'$ ,  $d\varsigma'$ ,  $d\varsigma'$ , and  $\nabla'$ . Let  $\rho'$ , the vector coordinate of any point, be supposed a function of an independent variable vector  $\rho$  (say the coordinate of the point's initial position), and  $t$  the time. Let  $u$  now stand for the reciprocal of the distance between two points in the  $\rho$  space, instead of as just now in the  $\rho'$  space. Similarly let  $U\nu$ ,  $ds$ ,  $d\varsigma$ , and  $\nabla$  refer to the  $\rho$  space. Finally, let  $\sigma = -\nabla_1 S\sigma'\rho'_1$ . Then instead of equation (32) we may write

$$4\pi(v+P) = \iint (v+P) S U\nu \nabla u ds + \iiint S \nabla u \nabla(\sigma'^2/2) d\varsigma \\ + \iint u \frac{dS U\nu\sigma}{dt} d\varsigma - \iiint u \frac{dS \nabla\sigma}{dt} d\varsigma. \quad (36)$$

# V. A particular Integral in the Theory of Elasticity.

Consider an elastically isotropic solid in equilibrium under arbitrary external bodily forces. Let  $\epsilon$  be the (small vector) displacement at any point. Also let  $\mathbf{F}$  be the external force per unit volume. Then [Thomson and Tait's 'Natural Philosophy,' § 698, equation (7)] the equation of equilibrium is

$$N\nabla^2\epsilon + M\nabla S\nabla\epsilon \equiv \psi\epsilon = \mathbf{F}; \quad . \quad . \quad . \quad (37)$$

where  $M, N$  have been put for Thomson and Tait's  $m, n$  respectively, and where  $\psi$  is a symbolic self-conjugate linear vector function of a vector,

$$\therefore \psi\omega = -T^2\nabla(N\omega - MU\nabla S\omega U\nabla),$$

we have

$$\psi^{-1}\omega = -T^{-2}\nabla\{N^{-1}\omega + (N^{-1} - [N + M]^{-1})U\nabla S\omega U\nabla\}.$$

[Here it is assumed that if

$$A\omega - BiSi\omega \equiv \psi\omega = \tau,$$

then

$$\tau = \psi^{-1}\omega \equiv A^{-1}\omega + (A^{-1} - [A + B]^{-1})iSi\omega,$$

which can be easily verified, if not obvious, by operating on the last equation by  $\psi$ . Therefore by equation (37),

$$\epsilon = \psi^{-1}\mathbf{F} = N^{-1}\nabla^{-2}\mathbf{F} - MN^{-1}(M + N)^{-1}\nabla^{-1}S\nabla^{-1}\mathbf{F}. \quad . \quad (38)$$

By equation (5) a particular value of  $\nabla^{-2}\mathbf{F}$  is given by

$$4\pi\nabla^{-2}\mathbf{F} = \iiint u\mathbf{F} \, ds;$$

and the integration may be supposed extended over the given region, or, in addition, over any external region where  $\mathbf{F}$  may be given any convenient values. Again,

$$4\pi\nabla^{-1}S\nabla^{-1}\mathbf{F} = 4\pi\nabla^{-1}S\nabla\nabla^{-2}\mathbf{F} = \nabla^{-1}S\nabla\iiint u\mathbf{F} \, ds = \iiint S\mathbf{F}\nabla \cdot \nabla^{-1}u \, ds.$$

Since we are seeking only a particular solution any particular value of  $\nabla^{-1}u$  will serve. Putting  $\sigma$  for the  $\rho_s - \rho_a$  of equation (4), it is known that

$$\nabla U\sigma = -2u,$$

so that

$$\nabla^{-1}u = -U\sigma/2.$$

Hence

$$8\pi N(M + N)\epsilon = \iiint \{2(M + N)u\mathbf{F} + MS\mathbf{F}\nabla \cdot U\sigma\} \, ds. \quad (39)$$

is a particular solution of equation (37).

If these symbolic methods be objected to—though they are just as legitimate as the ordinary symbolic methods adopted for discovering particular solutions—they may be regarded as

*Phil. Mag.* S. 5. Vol. 33. No. 205. June 1892. 2 L

furnishing only a hint of a particular solution, and the very easy verification that equation (39) really is a particular solution of equation (37) may follow.

This form of the particular solution is not the same as Thomson and Tait's ['Natural Philosophy,' § 731, equation (19)], and, for aught that appears above, may be a particular solution different from theirs. It is, however, the same as theirs. To verify this, express  $\mathbf{SF}\nabla \cdot \mathbf{U}\sigma$  in terms of  $\mathbf{F}$  and  $u^{-2}\mathbf{SF}\nabla \cdot \nabla u$ , thus:—

$$\mathbf{SF}\nabla \cdot \mathbf{U}\sigma = \mathbf{SF}\nabla \cdot (u\sigma) = -u\mathbf{F} + \sigma\mathbf{SF}\nabla u,$$

$$\mathbf{SF}\nabla \cdot \nabla u = -\mathbf{SF}\nabla \cdot (u^3\sigma) = u^3\mathbf{F} - 3u^2\sigma\mathbf{SF}\nabla u.$$

Eliminating  $\mathbf{SF}\nabla u$ ,

$$\mathbf{SF}\nabla \cdot \mathbf{U}\sigma = -\frac{2}{3}u\mathbf{F} - \frac{1}{3}u^{-2}\mathbf{SF}\nabla \cdot \nabla u.$$

Equation (39) thus becomes

$$24\pi N(M+N)\epsilon = \iiint \{2(2M+3N)u\mathbf{F} - Mu^{-2}\mathbf{SF}\nabla \cdot \nabla u\} ds, \quad (40)$$

the form given by Thomson and Tait.

Thomson and Tait regard this particular solution as the solution of the statical problem for an infinite solid. In this case some law of convergence must apply to  $\mathbf{F}$  to make these integrals convergent. Thomson and Tait ('Natural Philosophy,' § 730) say that this law is that  $\mathbf{F}r$  (where  $r$  is the distance from some arbitrary origin at a finite distance) converges to zero at infinity. This, I think, can be disproved by a particular case. Put, from  $r=0$  to  $r=a$ ,  $\mathbf{F}=0$ ; and from  $r=a$  to  $r=\infty$ ,  $\mathbf{F}r=r^{-n}\mathbf{a}$ ; where  $\mathbf{a}$  is a constant vector, and  $n$  is a constant positive scalar less than unity. Equation (39) then gives for the displacement at the origin, due to the part of the integral extending throughout a sphere whose centre is the origin and radius  $R(>a)$ ,

$$\epsilon = \frac{M+3N}{3N(M+N)} \frac{R^{1-n} - a^{1-n}}{1-n} \mathbf{a}.$$

Putting  $R=\infty$ , we get  $\epsilon=\infty$ . The real law of convergence does not seem to be worth seeking, as the practical utility of equations (39), (40) is owing to the fact that either of them is a particular integral for a finite body.

#### VI. *The Transference of Energy through an Electric Field.*

What follows is generalized in a paper about to be published. It is given here, as it will probably, even in the



particular form, interest such physicists as listen to the paper.

Prof. Poynting's theories of the transference of energy through an electromagnetic field are to-day universally known. In the Philosophical Transactions, 1884, part ii. pp. 343 to 349, he attempts to prove that the energy in the field has a time-flux  $\tau$  given by

$$4\pi\tau = \mathbf{V}\mathbf{E}\mathbf{H}, \quad . . . . . (41)$$

where  $\mathbf{E}$  and  $\mathbf{H}$  are the electromotive and magnetic forces respectively. In the Brit. Assoc. Reports, 1885, pp. 151, 152, Prof. J. J. Thomson points out that Prof. Poynting's reasoning is open to criticism; and that  $\nu$ , given by  $\nu = \tau + \mathbf{V}\nabla\sigma$  (where, if  $\sigma$  is discontinuous at any surface, the tangential component is not so) will serve equally well, if assumed to be the time-flux of energy, according to Prof. Poynting's reasoning, to explain the known facts. Put  $4\pi\sigma = \Psi\mathbf{H}$ , where  $\Psi$  is the electrostatic potential. [Note that, in order that this value of  $\sigma$  may satisfy the surface-conditions just mentioned,  $\Psi$  must be continuous.] We get as the time-flux of energy,

$$4\pi\nu = 4\pi\tau + \mathbf{V}\nabla(\Psi\mathbf{H}) = \mathbf{V}(\mathbf{E} + \nabla\Psi)\mathbf{H} + 4\pi\Psi\mathbf{C},$$

where  $\mathbf{C}$ , the current, is put in place of  $\mathbf{V}\nabla\mathbf{H}/4\pi$ . Substituting from equation (10) § 599 of Maxwell's 'Electricity and Magnetism,' viz.

$$\mathbf{E} = \mathbf{V}\mathbf{G}\mathbf{B} - \partial\mathbf{A}/\partial t - \nabla\Psi,$$

where  $\mathbf{G}$  is the velocity of matter at the point in question, we see that for a *steady* field,

$$\nu = \Psi\mathbf{C}; \quad . . . . . (42)$$

so that, assuming  $\nu$  instead of  $\tau$  to be the true time-flux of energy, in this matter of the transference of energy through the field, as in so many other respects,  $\mathbf{C}$  the current and  $\Psi$  the potential are the exact analogues of a liquid current and the pressure. Compare this with the very different conclusion of Prof. Poynting (Phil. Trans. 1884, part ii. p. 361:)—“I think it is necessary that we should realize thoroughly that, if we accept Maxwell's theory of energy residing in the medium, we must no longer consider a current as something conveying energy along the conductor.” According to the present result, in a steady field the sole means of conveyance of energy would be precisely the means Prof. Poynting warns us against, namely the electricity itself.

LVII. *On the Construction of a Colour Map.*  
 By WALTER BAILY, M.A.\*

[Plate VIII.]

**B**Y the term Colour Map I mean a diagram each point of which defines by its position some particular colour. Such a colour map was designed by Clerk Maxwell in the form of a triangle, the angles of which were occupied by certain colours, and all other colours were treated as mixtures of these three primary colours, the composition of the mixture for the colour which occupied any particular point in the triangle being indicated by the length of the perpendicular from that point on the sides of the triangle.

Now trilinear coordinates, although they afford very elegant methods for the solution of certain problems, are by no means so generally useful or so intelligible as the ordinary rectangular coordinates; and the fact that every colour can be defined by means of a spectrum colour and white light suggested to me the construction of a colour map with rectangular coordinates, in which measurement in one direction should indicate the wave-length of the spectrum colour employed and measurement at right angles to it should indicate the quantity of white light employed in defining the colour.

Let us take a vertical line to represent the spectrum, the lower end giving the red of the spectrum and the upper the violet. The spectrum is supposed to be formed so that equal differences of length measured along the spectrum represent equal differences in the wave-length; and when the quantity of colour at any point of the spectrum is mentioned it is intended that a definite small part of the spectrum about that part is to be taken. Now all colours, except the purples, can be formed by adding white light to a spectrum colour. Let the amount of white light required be indicated by a line measured horizontally to the right from the proper point in the spectrum. Then the given colour is indicated by the point at the extremity of that line. Again, every colour except the greens has the following property: viz. that if it is added in the proper quantity to some spectrum colour, white is produced. Let the quantity of white produced be indicated by a line drawn from the proper point horizontally to the left. The point at the extremity of this line indicates the given colour. In this way a map is obtained in which every colour has its appropriate position. The greens occur only on the right hand, and the purples only on the left hand, but all

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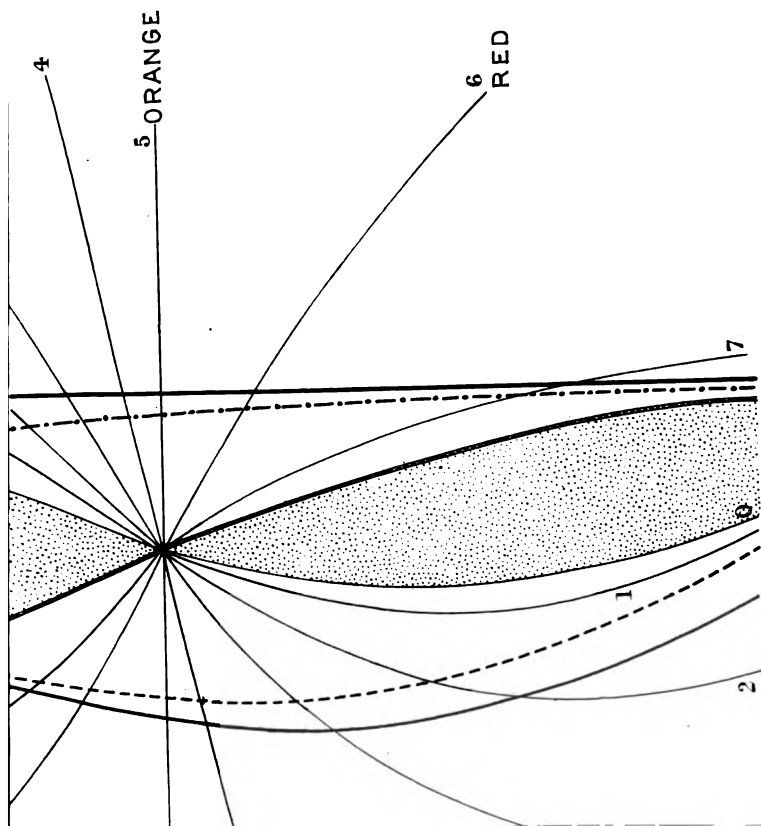


Fig. 5.



other colours, as they can be indicated in both ways, occur on both sides of the spectrum line.

In using the term quantity of white light, I mean that a beam of white light is to be obtained in some definite manner from a definite source of light which forms the spectrum, and that the map is to show how much of this beam is used. Captain Abney finds that the positive pole of the electric arc is a source of light of constant quality, and uses it in his measurements; and he indicates the quantity of white light used by the ratio between its luminosity and that of the spectrum colour. It is a more complicated matter to express such a ratio than to express the amount of white light only, and I failed to work into a map Captain Abney's method of defining the quantity of white light.

The principle on which this map is founded will come out more clearly by the consideration of fig. 1, which may be considered as a sort of colour staff, to borrow a term from music.

The three horizontal lines represent the three colour sensations—Red, Green, and Violet, with such luminosity that the mixture represented by equal lengths of the three lines represents white light. Thus the vertical lines A, A', wherever they may be placed, will include between them white light, which will be the more intense the farther they are apart. Any colour whatever may be represented by taking the line A as a base and measuring off the quantities of the sensations to points, R, G, and V. The distances included between A'

Fig. 1.

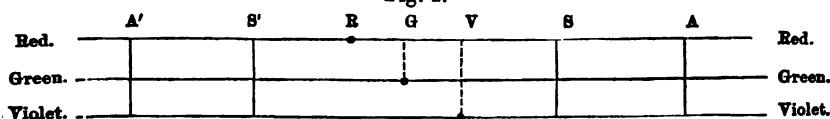


Fig. 2.

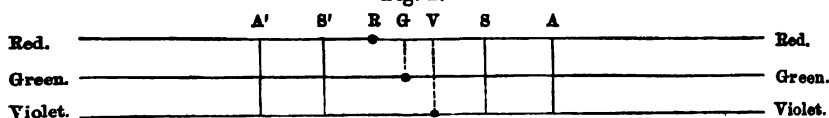
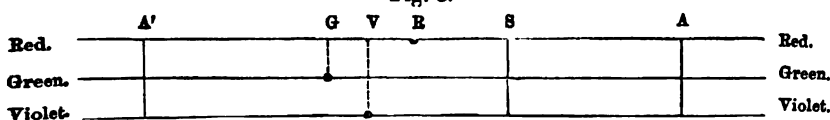


Fig. 3.



and R, G, V give every complementary colour to that represented by R, G, V, and A. The whole of the colours of this system are related together only by the position with respect

to one another of R, G, V—that is, only by the differences R G and G V. But if we express the same colours at (say) half the luminosity, we must reduce all these distances to one half, as in fig. 2, and so with any other proportion. It is then not the differences R G and G V, but the ratio of these differences which is constant for all this system of colours. Hence, to determine to what system a colour belongs of which we know  $r$ ,  $g$ ,  $v$ , the quantities of red, green, and violet sensations respectively, we have only to obtain  $\frac{r-g}{g-v}$ .

In fig. 4, Pl. VIII., the vertical line called “spectrum colours” is that along which the spectrum is thrown; and the lines called “line of no Red,” “line of no Green,” and “line of no Violet” are lines to which distances are to be measured horizontally from any point to show the quantity of red, green, and violet sensations in the colour represented at that point. When these distances are measured from points on the spectrum line, they give the amount of such sensation for the corresponding spectrum colour. The curves which I have used are not intended to represent the true form of such curves, as it is sufficient for explaining the principles of the map that they should be curves having a maximum and shading off on each side. The numbers marked along the “spectrum line” give the value of the fraction  $(r-g)/(g-v)$  at each point; and it will be seen that the value is large at the red end of the spectrum, probably beginning with infinity, and diminishes to zero, where the red and green are equal. It then changes sign and remains negative until  $g$  and  $r$  become equal, when the fraction becomes infinite and again changes sign. For the remainder of the spectrum the fraction continues positive and passes from infinity to zero. The fraction  $(r-g)/(g-v)$ , which may be called the “Colour Index,” has therefore in the spectrum every value from plus to minus infinity, and has all the positive values twice over. Every positive colour index has two spectrum colours:—one in which the order of magnitude of the sensations is Red, Green, Violet, and the other in which the order is Violet, Green, Red. In fig. 1, where the order is that required, let the lines S, S' give the spectrum colours. Then it is clear that these two spectrum colours are complementary to one another. Also that the colour represented by A is equal to the spectrum colour S plus the colour included between S and A, which is white; and also that the colour at A plus the spectrum colour at S' form the white between A and S'.

Now suppose the colour index negative, then R, G, V must be arranged in the order R V G or V R G (see fig. 3). We

have A, A', and S, as before; but S', the second spectrum colour, does not occur, inasmuch as there is no spectrum colour in which green is less than both the red and the violet. Hence the green, which is represented by A, can be defined only by the addition of white to a spectrum colour; and the purple, which is represented by A', can be defined only by the fact that when added to a spectrum colour they can form white.

To see how what precedes is represented in the Colour Map (Plate VIII. fig. 4), take any line perpendicular to the spectrum-line, say the line in the orange for which the Colour Index is 1.0, and compare this line with fig. 1. S is the point on the spectrum-line, V is the point at which the "line of no violet" is crossed, and G and R the points in which the lines of no green and no red respectively are crossed, and S' represents the complementary spectrum colour, which is represented on the thick line at the point marked 1.0. This thick line, along which the figures are marked, represents the spectrum which is complementary to that from Red to Yellow, and itself extends from Violet, of which the colour index is zero, to Blue, of which the colour index is infinite. A similar line gives the complementary spectrum of the part from Blue to Violet, and itself extends from Red when the colour index is infinite to Yellow when it is zero. The region on the right outside *all* the lines gives all the colours to be obtained by adding white to a spectrum colour; and to ascertain the amount of each sensation, we have only to measure horizontally to the line giving the zero of that sensation. The region on the left outside *all* the lines gives all the colours capable of making white with spectrum colours; and here, again, to ascertain the amount of each sensation we have only to measure horizontally to the line giving the zero of that sensation. It will thus be seen that the whole map is really constructed on one single principle. It is obvious that if a series of colours are obtained by some definite law, their positions on the map will lie on some line straight or curved.

It remains to consider the spaces enclosed within the lines. On the right between the spectrum-line and the nearest sensation zero-lines lies a space which has a real meaning, as the points in it represent colours in which the sensations have certain positive ratios to one another; but these ratios give a more intense colouring than the spectrum colours themselves, and therefore such points cannot represent any colours which can be seen by a normal eye, because, as was known to Newton, every mixture of colours is more diluted than the spectrum colour which it most nearly resembles. This region may be

called an abnormal region. The colours it represents would be visible to eyes more or less colour-blind. There are two abnormal regions on the left of the figure between the complementary spectrum-lines and the red and violet zero-lines respectively.

The remaining portion of the map, viz. that lying *between* zero sensation lines, is of a different nature. At any point in this region the distances measured to the zero lines are not all in the same direction; so that one or two out of the three sensations must be considered to be negative. As no one possesses a negative colour sensation, the colours represented in this region are imaginary. This may be called the imaginary region. Though it has no physical meaning it will be found to have its value in connexion with the geometrical structure of the map. As an example of this, consider the complementary spectrum-lines. They end abruptly, leaving a gap opposite the green; but they may be continued across the gap in such a way as their general form seems to point, and this has been done in fig. 4, by continuing the complementary spectrum-lines until they meet in a cusp at the point on the right marked  $-1.0$ . This extension lies wholly in the imaginary and abnormal region, and may represent the missing complementary spectrum of green.

The map affords convenient methods for calculating the effect of mixing colours. Let a colour which has the sensation red, green, and violet in the proportion  $r_1, g_1, v_1$  be represented by  $r_1 | g_1 | v_1$ . Then, if we take two colours  $r_1 | g_1 | v_1$  and  $r_2 | g_2 | v_2$ , the mixture of these colours in the proportions  $l_1$  and  $l_2$  will give the result  $l_1 r_1 + l_2 r_2 | l_1 g_1 + l_2 g_2 | l_1 v_1 + l_2 v_2$ . The index of this colour is

$$\frac{l_1(r_1 - g_1) + l_2(r_2 - g_2)}{l_1(g_1 - v_1) + l_2(g_2 - v_2)}.$$

Let the spectrum colour having the same index be  $r | g | v$ . In order to find the quantity of white which must be added to this spectrum colour to produce the required colour, it is necessary that the luminosity of the colour should be altered to that luminosity at which the colour is represented in the map. This can be done by multiplying the coefficient of each sensation by the fraction  $(r - g) / \{l_1(r_1 - g_1) + l_2(r_2 - g_2)\}$  or one of the equivalent fractions. The resulting sensation coefficients are

$$\text{Red} \quad . \quad . \quad . \quad (l_1 r_1 + l_2 r_2)(g - v) / \{l_1(g_1 - v_1) + l_2(g_2 - v_2)\}.$$

$$\text{Green} \quad . \quad . \quad (l_1 g_1 + l_2 g_2)(v - r) / \{l_1(v_1 - r_1) + l_2(v_2 - r_2)\}.$$

$$\text{Violet} \quad . \quad . \quad (l_1 v_1 + l_2 v_2)(r - g) / \{l_1(r_1 - g_1) + l_2(r_2 - g_2)\}.$$



The coefficient of the white to be added to the spectrum colour is obtained while the colour lies on the right hand by subtracting  $r$  from the red coefficient above obtained, or by subtracting  $g$  and  $v$  from the other coefficients respectively. When the colour lies on the left hand, the white is obtained by adding  $r$  to the above red coefficient, or  $g$  and  $v$  to the green and violet coefficients respectively.

I have applied the formulæ given above to obtain the curves showing the results of adding together in any proportion two spectrum colours so related to each other that if the first is  $r | g | v$  the second is  $v | g | r$ . The index of the second colour being  $\frac{v-g}{g-r}$  is the reciprocal of the index of the first.

The curves obtained are shown in fig. 5. Consider the curve numbered 2. This is the locus of mixtures of the blue whose index is 2.0, and the yellow whose index is 0.5. The curve passes through these two points of the spectrum, giving the cases in which a zero quantity of one of the colours is taken; and every other mixture is indicated by some point on the curve joining these two points and lying to the right of the spectrum-line. In this figure the dotted horizontal lines occupy the positions where the indices are zero and infinity respectively, so that the portion of any curve which lies outside of them must be repeated again on the left side of the complementary spectrum-line. In curve No. 2 two small parts do lie outside the dotted lines, and, accordingly, these two parts are repeated to the left of the complementary spectrum-line. We have then the curve No. 2 in three separate portions, which it is not possible to connect physically, as the missing part of the curve lies in the imaginary and abnormal regions. But what is not possible for physics is easy for geometry. We cannot subtract one spectrum colour from another, but we can subtract the lines representing the sensations in one spectrum colour from the lines representing the sensations in the other spectrum colour; and so by subtracting one spectrum colour from the other in any proportions we can complete the curve No. 2 through the imaginary and abnormal regions and so obtain the complete and continuous curve. Curves Nos. 1 and 0 have no portion on the complementary side, but curves Nos. 3 and 4 have a considerable portion on that side. A new feature is shown when we take the locus numbered 5. This is got by combining the spectrum indigo, having index 1.0, with spectrum orange, having the same index. These are complementary colours. When added together in the proper proportion they produce white, and when added in any

other proportion they produce white plus whichever spectrum colour predominates. Hence the locus consists of horizontal straight lines through the two points in the spectrum line, going off to infinity, where the colour indicated is white, considered as a spectrum colour infinitely diluted with white light. Next consider curve No. 7. The main portion of the curve lies to the left, and starts from points in the complementary spectrum-line which indicate the spectrum colour chosen. The parts of this portion which lie outside the horizontal dotted lines are repeated to the right of the spectrum-line; the remainder, obtained by subtraction, lies wholly in the imaginary and abnormal regions. All these curves pass through a certain pair of points, as may be easily shown.

The first spectrum colour is . . .  $r | g | v$ .

The second is . . .  $v | g | r$ .

By subtraction of one from the other, we get a colour

$$r-v | \text{zero} | v-r.$$

The resulting colour has therefore no green, and has the red and violet equal in amount but opposite in sign. These conditions are satisfied at the two points shown in the figure.

In this figure the lines are drawn under the condition that the index of one spectrum colour is the reciprocal of the index of the other; but any number of other systems of lines might be drawn showing combinations of two spectrum colours, so that it is evident that every colour can be resolved into two spectrum colours in an infinite number of ways.

There are three regions in fig. 5 which are shaded to show that none of the curves pass through them. These regions might probably be filled up by curves drawn through points in the imaginary part of the complementary spectrum to which I have already alluded.

Now the complementary spectrum-line and the curves giving mixtures of two spectrum colours have been drawn by strict arithmetical methods from certain curves of hypothetical form which indicate the intensity of the sensations for each point of the spectrum; but they can also be plotted out by direct experiment.

To plot out the complementary spectrum-line, add to a spectrum colour its complementary until white is produced, measure the quantity of white, and mark off a horizontal line to the *left* from the point in the spectrum of a length proportional to the quantity of white. The end of this line is a point in the complementary spectrum; other points may be obtained in the same way, and the normal part of the complementary spectrum-line be drawn.

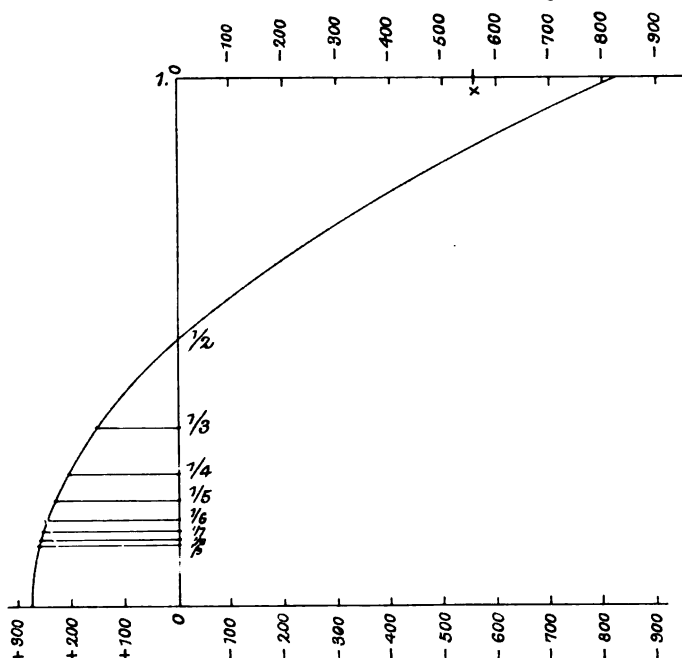


Fig. 1. *Primary curve of the Hydrogen Spectrum.*

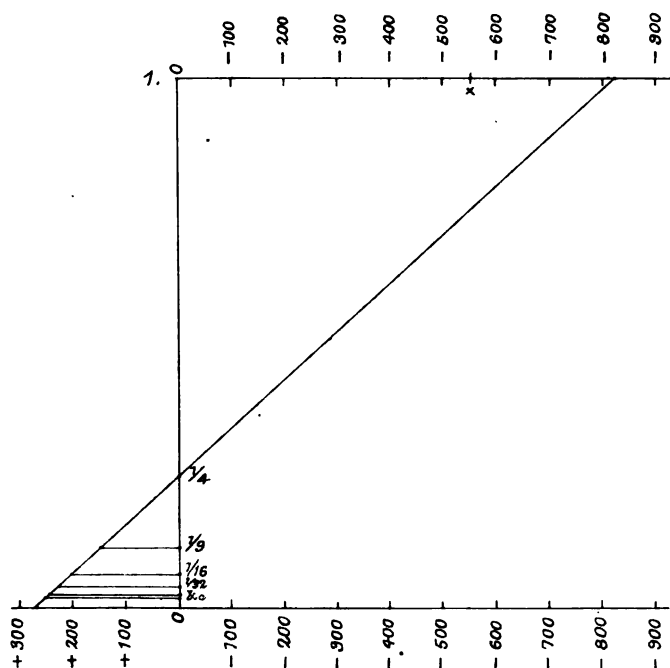


Fig. 2. *Derived curve of the Hydrogen Spectrum.*



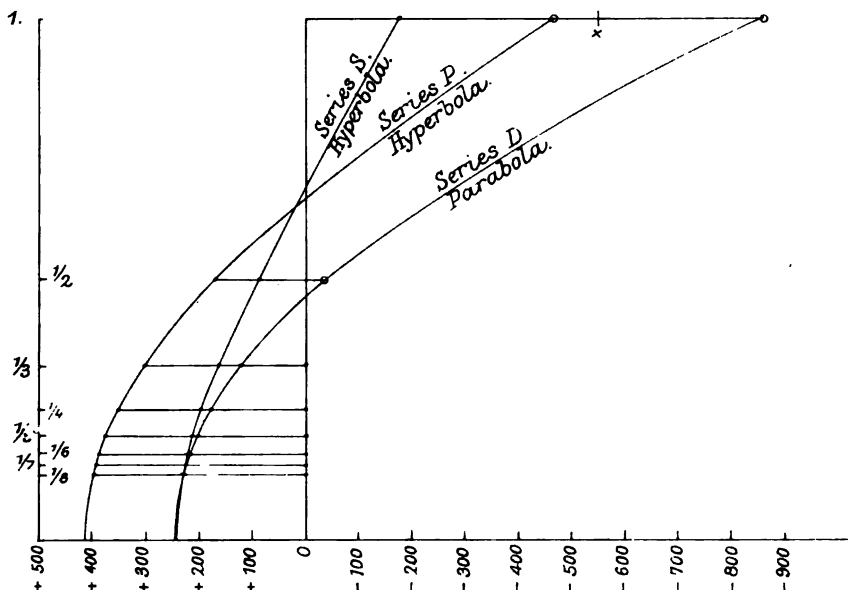


Fig. 4. The three Primary curves of the Spectrum of Sodium.

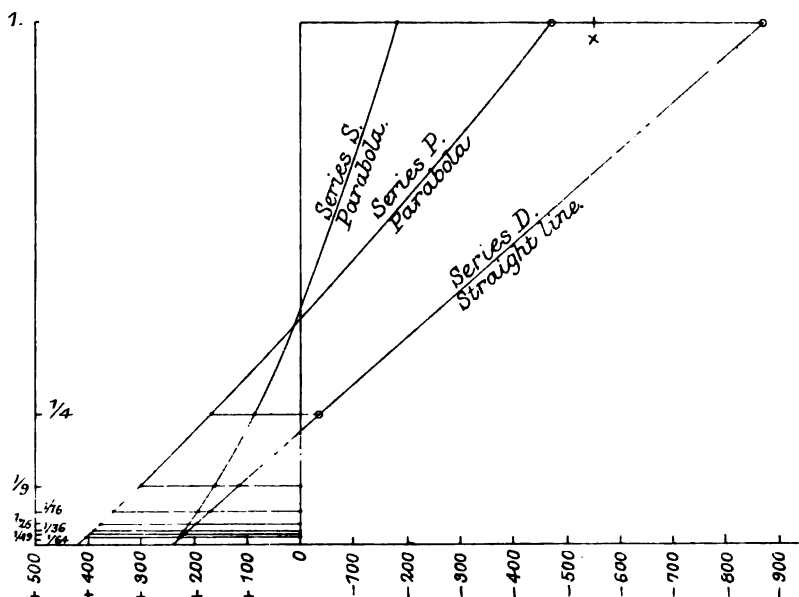


Fig. 5. The three Derived curves of the Spectrum of Sodium.



To plot out the curve giving the mixtures of two spectrum colours, take a third spectrum colour and make a colour patch of the first two colours, and another colour patch of the third colour and white. Keep the luminosity of the third colour constant, and vary that of the other colours and the white until both patches are of the same colour. Then measure the quantity of white used and mark off a line from the position of the third spectrum colour to the right proportional to the quantity of white. The end of this line gives a point in the curve. By taking other spectrum colours as the third colour other points may be obtained. If, however, it is found impossible to make the two patches of the same colour, then throw the three spectrum colours together, and keeping the luminosity of the third colour constant vary that of the other two until the three produce white; measure the quantity of white, and mark off to the left from the position of the third spectrum colour a line proportional to the quantity of white obtained. The end of this line is a point in the curve. If both these methods fail the point on the curve corresponding to the third spectrum colour lies in the abnormal or imaginary regions, and cannot be determined by experiment.

When the derived curves have been plotted out by experiment, it will be possible to modify the hypothetical forms of the curves of intensity of the sensation in the spectrum so as to make the curves derived from them accord more closely with the results of experiment, and so to arrive by gradual approximation to the true form of those curves.

LVIII. *Analysis of the Spectrum of Sodium, including an Inquiry into the true place of the Lines that have been regarded as Satellites.* By G. JOHNSTONE STONEY, M.A., D.Sc., F.R.S., Vice-President, Royal Dublin Society\*.

[Plates VI. & VII.]

*Introduction.*

**I**N analysing spectra, the following definitions and distinctions will be found of use:—

*j*, the *jot* of time, is the time that light takes to advance one tenth of a millimetre in the open æther. In the open æther all rays † travel this distance in the same time, which is approximately one third of the twelftheth (one

\* Communicated by the Author. From the Scientific Proceedings of the Royal Dublin Society, vol. vii. part 3.

† By a ray of light is meant the light producing a line in the spectrum.

third of the millionth of the millionth) of a second of time.

The *micro-jot* is the millionth part of a jot.

$j_1$  the *air-jot* of time, is the time that the ray of mean refrangibility takes to advance one tenth of a millimetre in air. Accordingly  $j_1 = \mu_1 j$ , where  $\mu_1$  is the refractive index of air for the ray of mean refrangibility. If we regard the ray whose wave-length is 5000 tenthmetres as the mean ray, then  $\mu_1$  is very nearly 1.000280. (See British Association catalogue of oscillation-frequencies in the Brit. Assoc. Report for 1878.)

$\lambda$  is the *wave-length-in-air* of a ray, expressed in tenthmetres, as determined by Rowland\*.

$\kappa$  is the "*inverse-wave-length*," i. e.  $10^8/\lambda$ . It is the number of wave-lengths-in-air which occupy one tenth of a millimetre.

$T$  is the *periodic time* of the waves of a ray of light, expressed in micro-jots. Hence  $T = \mu\lambda$ , in which  $\mu$  is the refractive index of air for the ray of wave-length  $\lambda$ .

$N$  is the *oscillation-frequency in each jot of time*, i. e. the number of the oscillations of the waves of a ray in each jot.  $It = \kappa/\mu$ .

Of these quantities  $N$  is obviously the one which is best adapted to theoretical investigation. It is, however,  $\lambda$  that is observed. From this  $\kappa$  can be accurately deduced, but  $N = \kappa/\mu$  cannot be accurately obtained till we know the value of  $\mu$  for different parts of the spectrum. We may, however, in a theoretical investigation, use, instead of  $N$ , any quantity proportional to it, e. g.  $\mu_1 N$ , where  $\mu_1$  has the value assigned to it above. We shall call this  $n$ . It is the oscillation-frequency in each "air-jot" of time. Accordingly

$$n \text{ is the oscillation-frequency in each air-jot of time. It} \\ = \mu_1 N = \kappa \cdot \mu_1 / \mu.$$

Now Ketteler's observations on the dispersion of air, though not sufficient for the general determination of  $\mu$ , are enough to satisfy us that  $\mu$  does not anywhere differ more than a *very* little from  $\mu_1$ , its mean value. And accordingly, in comparing our results with observation, we shall regard  $\mu_1/\mu$  as unity, and treat  $\kappa$  (the quantity furnished by observation) as if it were identical with  $n$  (the quantity required by theory). With this we must be content until adequate determinations

\*  $\lambda$  is accordingly about 1/8000th more than the wave-length as determined by Ångström.



of  $\mu$  for the various parts of the spectrum shall have been made.

*Method of Analysis.*

The spectrum of sodium, so far as it has been explored, consists of 14 pairs of lines, and of 8 others which have not yet been seen to be double. Professor Rydberg and Professors Kayser and Runge independently discovered that all the observed lines—with one remarkable exception—lie in three definite series, somewhat similar to that which Dr. Huggins had found in the Spectrum of Hydrogen; and they have worked out empirical formulæ which assign to the lines their places in these series. The kind of formula to be tried was suggested by Balmer's Law for the lines in hydrogen, viz.

$$n = k \left( 1 - \frac{4}{m^2} \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $k$  stands for the number 274·263. In this formula  $n$  becomes the oscillation-frequencies of the several hydrogen-lines, when for  $m$  we write in succession the positive integers 3, 4, 5, &c. For the spectra of the other light monads, including sodium, Rydberg made use of the form

$$n = A + \frac{B}{(m+h)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the quantities  $A$ ,  $B$ , and  $h$  have to be determined for each series. Kayser and Runge preferred the form

$$n = A + \frac{B}{m^2} + \frac{C}{m^4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the three constants to be determined for each series are  $A$ ,  $B$ , and  $C$ . Either formula can be made to agree tolerably with the observations, and sometimes in more than one way.

In a paper communicated last year to the Royal Dublin Society\*, the present author showed that each of the three series in the spectrum of sodium is due to the motion of an electron—a definite electric charge—within the molecules of sodium along an orbit; or at least to some event taking place within the molecules which follows the same mathematical laws as are furnished by such a motion of an electron. This motion may be resolved into its elliptic partials by Fourier's Theorem; and it is shown that each of these elliptic partials

\* Stoney, "On the Cause of Double Lines in Spectra," Scientific Transactions of the Royal Dublin Society, vol. iv. p. 563.

gives rise to a line in the spectrum, which will become a double line if the partial is exposed to an apsidal shift. It is also shown how the relative sizes, the forms, and other information about the partials may be obtained from the observations; and especially how the periodic time of each partial may be deduced from the positions of the two constituents of the double line to which it gives rise. It is found to be the periodic time which corresponds to the position midway between the two constituents of the double line on a map of oscillation-frequencies.

Now the periodic times of these partials are not simply a fundamental period and its harmonics, as is the case with the vibrations that produce musical notes. Balmer's Law, however, and the empirical formulæ that Rydberg and Professors Kayser and Runge have found to be suitable, suggest that they in some way depend on an event of that simple character. In fact this state of things is represented mathematically by  $n$  (the position of the line on a map of oscillation-frequencies) being a function (probably some simple function) of  $1/m$ ; which it is both in Balmer's Law and in the above-mentioned empirical formulæ.

In the case of the hydrogen spectrum this relation is conspicuously placed in evidence by a very simple diagram. For if we write  $y$  for  $1/m$ , and  $x$  for  $n$ , equation (1) becomes

$$y^2 = \frac{1}{4k} \cdot (k-x), \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which, if we regard  $x$  and  $y$  as running coordinates, is the equation of a parabola. Hence the following rule—Draw the foregoing parabola and place its axis horizontal. Erect an ordinate at the distance  $k$  from the vertex. Double this out, and, using its double length as unit, set off upon it the harmonics  $1/2$ ,  $1/3$ ,  $1/4$ , &c. From the points so determined draw horizontal lines to the curve: these are the values of  $n$  for the successive lines of the hydrogen spectrum, on the same scale on which the distance of the ordinate from the vertex represents 274.263, which is the value of  $k$  (see Plate VI. fig. 1).

Now, having regard to the fact that the light monad elements H, Li, Na, K, Rb, Cs have all of them series of double lines which appear to belong to the same general type, we are justified in assuming that Balmer's Law is the simplest case of a general law which prevails throughout all the light monads. Hence, if the oscillation-frequencies be all plotted down as the horizontal lines of a diagram constructed as above with  $x=n$  and  $y=1/m$ , the curve passing through the

ends of the horizontal lines in the other monads should be some curve of which the parabola is a particular case. This may happen in different ways, but the simplest hypothesis is that they are hyperbolas or ellipses. It appeared therefore to be worth ascertaining whether diagrams with hyperbolas or ellipses, instead of the parabola, would agree with the observed positions of the lines in one of the other monads. Sodium is the monad selected ; chiefly because of the peculiar pair of lines that present themselves in the spectrum of this element—which Rydberg speaks of as satellites, and which Kayser and Runge regard as probably belonging to a fourth series of lines, of which they are the only term that has been found. There seemed some ground for hoping that the inquiry would reveal the true significance of these lines.

A curve of the second degree, with the axis of  $x$  as one of its principal axes, can be drawn through any three assigned points. We have therefore to determine the ellipse or hyperbola that passes through three of the observed positions, and then to ascertain how far the other observed positions lie from that curve. The following lemma makes it easy to do this:—

*Lemma.*—When the  $y$ 's of a number of points are given (in this case the successive values of  $m$ ), so that the accurate values of  $y^2$  for the successive points can be obtained, we may use, instead of the ellipse or hyperbola, the curve derived from it by making the new ordinates proportional to the squares of the old ones. Thus the ellipse

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1,$$

and the hyperbola

$$\frac{x^2}{a^2} - \frac{y^2}{b^2} = 1,$$

furnish as their derived curves

$$\frac{x^2}{a^2} + \frac{z}{b^2} = 1, \text{ and } \frac{x^2}{a^2} - \frac{z}{b^2} = 1,$$

in which  $z$  must be positive. In other words, the derived curve is the *portion* on the upper (*i. e.* positive) side of the axis of  $x$ , of a parabola with its axis vertical. This parabola passes through the ends of the axis major of the ellipse or hyperbola. When derived from an ellipse its vertex is above the axis of  $x$ , under it when derived from an hyperbola. The parabola degrades into a straight line, if the curve from which it is derived is a parabola instead of an ellipse or hyperbola. Thus fig. 1 of Plate VI., when we substitute its derived

curve, viz.  $x=k(1-4z)$ , simplifies into fig. 2, in which, as before, the horizontal lines represent the oscillation-frequencies of the successive hydrogen rays.

Hence the problem to be solved is reduced to the easier problem of passing a parabola with its axis vertical through three given points.

For  $m$  we are to put in succession the positive whole numbers 1, 2, 3, 4, &c.; that is, for  $y$  we are to use the harmonic fractions 1,  $1/2$ ,  $1/3$ , &c., and for  $z$  the squares of these, viz. 1, .25, .1', .0625, .04, .027', .02040816, .015625, .012345679, .01, &c., or numbers proportional to them.

Some of these values may assign negative values to  $n$  (the oscillation-frequency). It has hitherto been assumed that it is only the positive values of  $n$  that need be attended to; that in fact the negative values do not correspond to lines in the spectrum. This seems to be a mistake: for the elliptic partial from which a line arises being (see Stoney, "On Double Lines," Sc. Trans. R.D.S., vol. iv. p. 570),

$$x = a \cos \left( \frac{2\pi n}{j_1} t \right),$$

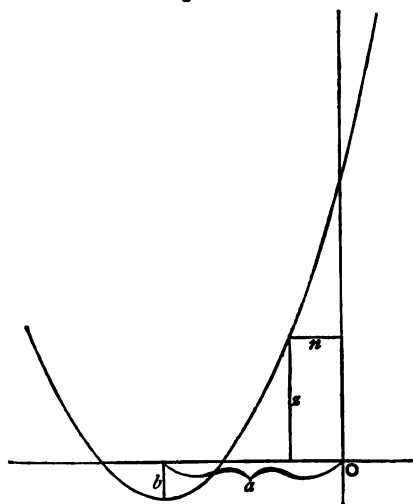
$$y = b \sin \left( \frac{2\pi n}{j_1} t \right),$$

the effect of changing the sign of  $n$  is simply to reverse the direction in which the electron travels round the ellipse. If the ellipse maintains a fixed position, this partial produces a single line in the spectrum, the position of which is the same whether  $n$  is positive or negative. If the ellipse is subjected to an apsidal shift during the flight of the molecule, the partial produces a double line in the spectrum (*loc. cit.*), the constituents of which either occupy the same positions when  $+n$  is changed into  $-n$ , or each simply exchanges place with the other. Which of these will happen depends on the direction of the apsidal motion, and on this we shall have something more to say further on (p. 515); but in either case the same two positions in the spectrum are occupied by the constituents of the double line. There is, however, one alteration the lines *must* undergo when  $n$  changes sign, viz. that what was before the more refrangible side of each line now becomes its less refrangible side. Now this accords with what we find to be indicated in the case of that outlying pair of sodium-lines that have been supposed to be satellites. While all other sodium-lines are more nebulous on the less refrangible side, the constituents of this particular pair are nebulous on the more refrangible side. We should therefore

be prepared for what we shall learn further on, viz. that this pair of lines is due to a negative value of  $n$ .

Before, however, we can draw the diagram for any of the series of lines, we are confronted at the outset with a difficulty. We have to settle what three points the curve is to pass through. This depends on what the number  $m$  is for the least refrangible line. It is 3 in the case of the hydrogen series, but there seems no reason to conclude with Kayser and Runge that it is 3 in other cases. A preliminary diagram was made on millimetric paper to help in determining this point. Each supposition as to the value of  $m$  in the least refrangible line furnishes a distinct set of points corresponding to the observed values of  $n$  for the terms of the series. It was easy to draw curves through the several sets plotted down in this way, and that set was preferred which most nearly agrees with the supposition that an ellipse or hyperbola takes the place of the parabola of the hydrogen series; or rather (since it was a diagram of the derived curves that was employed) that a parabola with its axis vertical takes the place of the straight line of the hydrogen series. This may be seen by inspection in some cases. In others it cannot be so determined, and it was necessary to have recourse to the calculation by which a parabola is passed through three of the points, and by which the deviations of the other points from the parabola are computed. The case in which these deviations proved to be smallest is the one finally selected.

Fig. 8.



If the curve furnished by the relation between  $n$  and  $y$  is an hyperbola, the derived curve (representing the relation between  $n$  and  $z$ ) is the part above the axis of  $n$  of a parabola such as that represented in fig. 8, its equation being

$$(a-n)^2 = P(b+z), \quad \dots \quad (5)$$

*Phil. Mag.* S. 5. Vol. 33. No. 205. June 1892. 2 M

in which  $n$  and  $z$  are the running coordinates,  $P$ ,  $a$ , and  $b$  being determined by the condition that the parabola shall pass through three given points, suppose

$$n_1 z_1, \quad n_2 z_2, \quad n_3 z_3.$$

We easily find that this condition is fulfilled if

$$\left. \begin{aligned} P &= \frac{n_3 - n_1}{\frac{z_1 - z_3}{n_3 - n_1} - \frac{z_2 - z_3}{n_3}} \\ 2a &= P \frac{z_1 - z_3}{n_3 - n_1} + n_1 + n_3 \\ b &= \frac{(a - n_1)^2}{P} - z_1. \end{aligned} \right\} \dots \dots \dots (6)$$

[Similarly, if the relation between  $n$  and  $y$  were such as to be represented by an ellipse, the derived curve would have the equation

$$(a + n)^2 = P(b - z), \quad \dots \dots \dots (7)$$

in which, as before,  $P$ ,  $a$ , and  $b$  can be determined so as to make the curve pass through three given points.]

The hyperbola, of which equation (5) is the derived curve, is of course

$$(a - n)^2 = P \cdot (b + y^2); \quad \dots \dots \dots (5a)$$

and the ellipse corresponding to equation (7) is

$$(a + n)^2 = P(b - y^2), \quad \dots \dots \dots (7a)$$

in which  $n$  and  $y$  are the running coordinates.

These are equivalent to

$$(a - n)^2 = P \left( b + \frac{1000}{m^2} \right), \quad \dots \dots \dots (5b)$$

and

$$(a + n)^2 = P \left( b - \frac{1000}{m^2} \right), \quad \dots \dots \dots (7b)$$

which give directly the relation between  $m$  and  $n$ , when for  $z$  we use 1000 times the values on page 508.

#### *Application to Series P.*

Series P appears to be best represented by regarding the least refrangible pair of the series—the great D lines of the solar spectrum—as corresponding to  $m=2$ . The values of  $m$  for the other lines will then be as in the following Table:—

$m.$	$z = \frac{1000}{m^2}$	$x = \pm x$ (which is nearly the same as $n$ ), by observation.
1	1000.0	Not yet observed.
2	250.0	169.6878
3	111.1'	302.7762
4	62.5	350.5193
5	40.0	373.0703
6	27.7'	385.5080
7	20.40816	393.1049
8	15.625	398.0527

The Table also gives the values of  $x$  (by observation) and of  $z$  (by calculation) of the derived curve. If we pass a parabola with its axis vertical through three of these points, viz. through:—

$$z_2 = 250, \quad z_3 = 111.1', \quad z_6 = 27.7',$$

$$x_2 = 169.6878, \quad x_3 = 302.7762, \quad x_6 = 385.5080,$$

we find, by the method of the last paragraph, that

$$\log P = 3.774,0300,$$

$$a = 3337.4120,$$

$$b = 1438.35.$$

Putting these values into equation (5) and computing the values of  $n$  (i. e.  $x$ ) for the other terms of the series, we find:—

$m.$	$n$ calculated.	$x$ by observation (which is nearly the same as $\pm n$ ).	Difference.
1	-469.4	Not yet observed.	Unknown.
2	Used for determining the constants.		0.00
3	Used for determining the constants.		0.00
4	+350.767	350.519	+0.25
5	+373.239	373.070	+0.17
6	Used for determining the constants.		0.00
7	+392.945	393.105	-0.16
8	+397.776	398.053	-0.28

Accordingly all the observed points lie nearly on this parabola. The parabola is in the position shown in fig. 3, from which it follows that the primary curve (which represents the relation between  $n$  and  $1/m$ ) is a curve which is nearly a hyperbola. See Pl. VII. figs. 4 and 5.

*Application to Series D.*

Series D is best represented by a straight line for its derived curve, and accordingly by a parabola for its primary curve. Putting as before  $x=n$  and  $z=1000/m^2$ , and taking

$$x = a - \alpha z$$

as the equation of the derived curve, in which

$$a = 244.93 \quad \text{and} \quad \log \alpha = .04357,$$

and computing the successive terms, we find:—

$m$ .	$n$ calculated.	$\pm \kappa$ by observation (which is nearly the same as $n$ ).	Difference.
1	-860.6	Too far in ultra-violet for observation.	
2	- 81.17	Too far in ultra-red for observation.	
3	+122.093	+122.036	+0.057
4	+175.834	+175.884	-0.050
5	+200.709	+200.746	-0.037
6	+214.221	+214.256	-0.035
7	+222.368	+222.363	+0.005
8	+227.656	+227.676	-0.020

results which show that the primary curve of Series D approximates very closely indeed to a parabola. See Pl. VII. figs. 4 and 5.

*Application to Series S.*

This is the most interesting of the series so far as the present inquiry is concerned, because it is the series to which belongs the outlying double line which has been supposed to be a satellite of one of the terms of Series D.



If we regard this particular line as the first term of the series, it will be found that the primary curve belonging to the series closely approximates to an hyperbola. If we regard that line as the second term, the curve approximates, but not so closely, to an ellipse. We shall therefore adopt here the former supposition. The values of  $m$  will then be as in the following Table :—

$m.$	$x = \frac{1000}{m^2}.$	$x = \frac{1}{n}$ (which is nearly the same as $n$ ), by observation.
1	1000.0	—176.2686
2	250.0	+ 87.5500
3	111.1'	+162.3935
4	62.5	+194.1200
5	40.0	+210.5142
6	27.7'	+220.0515
7	20.40816	+226.1441
8	15.625	+230.2185

The coordinates in the Table are coordinates of the derived curve. It is approximately a parabola in the position of fig. 3. Taking equation (5) as its equation, the constants are to be determined by the condition that the parabola shall pass through three of the observed points, suppose through

$$\begin{aligned} z_1 &= 1000, & z_3 &= 111.1', & z_6 &= 27.7', \\ x_1 &= -176.2686, & x_3 &= 162.3935, & x_6 &= 220.0515. \end{aligned}$$

Using these values in equations (6), we find

$$\begin{aligned} \log P &= 2.526,3843, \\ a &= 434.0587, \\ b &= 108.514, \end{aligned}$$

and computing the values of  $x$ , i. e.  $n$ , for the other terms, we get:—

<i>m.</i>	<i>n</i> calculated.	<i>n</i> by observation (which is nearly the same as $\pm n$ ).	Difference.
1	Used for determining the constants.		0
2	+ 86.966	87.550	-0.58
3	Used for determining the constants.		0
4	+194.337	194.120	+0.22
5	+210.662	210.514	+0.15
6	Used for determining the constants.		
7	+225.919	226.144	-0.22
8	+229.816	230.218	-0.40

*Inferences.*

From the whole investigation we may draw the following inferences :—

1. That the outstanding differences are sufficiently large to warrant the conclusion that the primary curve is not an exact curve of the second degree, although in the case of Series P it approximates to an hyperbola ; in the case of Series S to an hyperbola or ellipse, probably to an hyperbola ; and to a parabola in the case of Series D.

2. That the approach to the parabola is very close in the case of Series D, but that in the case of Series P and in the case of Series S the actual curve, as indicated by the observations, is somewhat more curved in the vicinity of its vertex than is the hyperbola which approximates to it.

3. That the double line which has been regarded by Rydberg as a satellite of one of the terms of Series D, and by Kayser and Runge as belonging to a fourth series, is in reality the first, or the second, term of Series S—the first, if the primary curve of Series S is of a hyperbolic form ; the second if it is elliptic.

4. That negative values of *n* furnish real lines in spectra, of which the double line spoken of above is an instance.

5. That in Series P the term corresponding to *m*=1 has a negative value for its *n*, viz. -469.4, approximately corresponding to wave-length  $\lambda=2130$ . This is perhaps not at too great a distance in the ultra-violet to be observed, if the line have sufficient intrinsic brightness. Professor Hartley has succeeded in photographing as far as  $\lambda=1800$ .

6. That in Series D there are two new terms corresponding to negative values of  $n$ , for one of which  $n$  is approximately  $-860.6$ , and for the other  $-31.17$ . These positions are the same as  $\lambda=1162$ , and  $\lambda=32082$ . The first of these is probably too far in the ultra-violet and the other much too far in the ultra-red, to be observed.

7. Similarly, in the hydrogen spectrum there seems to be a new line in the ultra-violet, viz. the line obtained by putting  $m=1$  into Balmer's formula. This makes  $n=-822.789$ , which is the same as  $\lambda=1215$ , a position, however, which is probably too far removed in the ultra-violet for observation.

8. Lines corresponding to negative values of  $n$  do not appear to have been observed in any of the monad elements except sodium, but examples of them are met with in some of the triple-line series of the dyads. Kayser and Runge record what is presumably one triple group of this kind in the spectra of zinc, cadmium, and mercury, and what is perhaps a second group in the spectra of zinc and cadmium (see the photographs they give of a part of each of these spectra, and the observations they make about them on p. 71 of their fourth Paper, *Ueber die Spectren der Elemente*, in the Transactions of the Berlin Academy for 1891).

It is not yet known what kind of perturbation within the molecules would be competent to affect the partials of the undisturbed motion of an electron so as to resolve the resulting lines into triple lines. But it is, nevertheless, suggestive to find that in the spectra of Zn, Cd, and Hg the constituents of the triple line corresponding to a negative value of  $n$  are not reversed, but in the same relative positions to one another as are those furnished by positive values of  $n$ . If this non-reversal of position prevails among those double lines of sodium which are due to negative values of  $n$ , it will probably be indicated by the less refrangible constituent of the double line, No. 1 of Series S, being the brighter, as is said to be the case with the double lines of the same series, which are due to positive values of  $n$ . This would imply a physical fact of importance, viz. that a change in the sign of  $n$  induces a change in the direction of the apsidal perturbation as well as in the direction of revolution in the elliptic partial. If, on the other hand, it is found that the more refrangible constituent of the double line is the stronger, this will go far to prove that the direction of the apsidal shift is independent of the sign of  $n$ . It is therefore desirable to ascertain by observation which constituent is the brighter.

9. Finally, our investigation makes it probable that there is some connexion between Series D and Series S in the

spectrum of sodium, and that the same relation prevails between the two series of triple lines in the spectra of Zn, Cd, and Hg. This is suggested by the circumstance that the line which we now know to be the first term of Series S stands in a position in all these spectra which appears to be related in the same way to the positions in them of the lines of Series D. But what the connexion is we do not yet know.

### *Description of the Diagrams.*

A sketch on a very small scale of the primary curves of the three sodium series is given in Plate VII. fig. 4, and a sketch of their derived curves is given in fig. 5. In both these figures, as in the diagrams of the corresponding hydrogen curves in Plate VI., the horizontal lines represent the oscillation-frequencies of the successive lines of each series, when measured from the vertical line to the curve belonging to that series. A small circle is placed round those dots that correspond to lines that have not yet been observed, and the cross on the upper line between  $-500$  and  $-600$  indicates the distance to which Professor Hartley has succeeded in photographing in the ultra-violet.

To judge what the approximation is that has been obtained, imagine each of the diagrams enlarged, until the vertical line becomes ten metres long. Each of the diagrams would then occupy the side of a large house. Even on this immense scale the greatest deviation of the observed ends of the horizontal lines from the curve would be less than six millimetres in the case of Series S, would be under three millimetres in Series P, and would be only a fraction of a millimetre in Series D. Although these deviations are very small, modern spectroscopic work is carried out with such accuracy that they may not be attributed to errors of observation, and, accordingly, we are justified in drawing the first and second of the inferences on p. 514.

LIX. *A Note on the Electromotive Forces of Gold and of Platinum Cells.* By E. F. HERROUN, *Professor of Natural Philosophy in Queen's College, London*.\*

IN nearly all modern text-books of Physics the metal platinum is placed after gold in Volta's Electropositive Series. This no doubt is partly owing to the well-known fact that gold is attacked by chlorine or nitrohydrochloric acid more readily than platinum, and it might therefore be

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reasonably supposed that gold evolves more heat in the formation of its chloride than does platinum. On referring to the values for the heats of formation of the chlorides of these two metals, as given by Julius Thomsen\*, one finds, however, that the heat attending the formation of auric chloride is, per equivalent, only about half as great as that in the case of platinic chloride.

Assuming that the voltaic constants of metals are deducible from the thermochemical values of their compounds, the above facts would compel us to regard gold as more negative than platinum, at least when immersed in chloride solutions. (The same observations would also apply if oxygen were the attacking medium, as Thomsen gives the heat of formation of platinic hydrate as a considerable positive number, while that of auric hydrate is a large *negative* quantity.)

It was, therefore, an interesting point to determine how far the actual electromotive forces obtained with gold and with platinum agreed with these conclusions, and I endeavoured to find records of the electromotive forces of cells in which these metals are immersed in solutions of their chlorides opposed to some other metal in a solution of its corresponding salt. While there are many references to the E.M.F.'s set up in single fluid cells in which platinum is one of the metals used, the references to gold are scanty, and even with platinum I have only succeeded in finding one recorded measurement in which the platinum was immersed in a solution of its own salt. This was a measurement made by Wheatstone†, in which liquid zinc amalgam was opposed to platinum in a solution of platinic chloride. He found in measuring the E.M.F. of this cell that it required 40 turns of his rheostat, as compared with 30 turns required for a form of Daniell cell. Now, assuming his Daniell cell to have had an E.M.F. of 1.09 volt, the value in volts for the zinc amalgam, platinum-platinic chloride cell would be 1.453.

In a list of the potential differences between different metals and graphite simply immersed in water, Götz and Kurz‡ give the values 0.48 volt for gold and 0.37 volt for platinum, the value for zinc and graphite being 1.37 volt. This would make platinum more electronegative than gold by 0.11 volt; but these values cannot be accepted as in any degree expressing the actual electromotive forces concerned.

Exner and Tuma§, on the other hand, taking carbon = 0,

\* *Thermochemische Untersuchungen*, iii. pp. 412 & 430.

† Wheatstone's *Scientific Papers*, p. 115.

‡ *Electrotechnie Zeit.* ii. p. 30.

§ *Wien. Ber.* xcvii. p. 917.

give  $Pt = 0.05$ ,  $Au = -0.05$ , which appear to be much more probable values, and make gold, as its thermochemical data require, negative as regards platinum.

Under these circumstances it appeared worth while measuring the actual E.M.F. set up between zinc and gold, and zinc and platinum, in solutions of their own chlorides of equal molecular strength.

#### *Zinc-Platinum Cell.*

The heat of formation of  $PtCl_4$  is apparently unknown, but as it appears to be impossible to prepare a *neutral* solution of that salt, compounds such as  $PtCl_4 \cdot 2HCl$  or  $PtCl_4 \cdot 2NaCl$  must be substituted, and their heats of formation are given by Thomsen. I selected the latter salt on account of its freedom from acid, and prepared a neutral solution having the strength of  $\cdot 25 (PtCl_4 \cdot 2NaCl) 100H_2O$ , which therefore contained about 2.75 grams of Pt in 100 cub. centim. of solution.

Thomsen gives for  $[PtCl_4 \cdot 2NaCl, aq]$  the value 73720 + 8540 = 82,260 calories; and for  $[ZnCl_2, aq]$  the value 112,840 calories. These numbers would give as the heat of replacement of one equivalent of platinum by zinc the nett heat evolution of 35,855, which is equivalent to a theoretical E.M.F. of 1.548 volt.

A cell was set up consisting of an amalgamated pure zinc rod immersed in a solution of  $\cdot 25 ZnCl_2 \cdot 100H_2O$ , opposed to a clean platinum plate immersed in the solution of sodio-platinic chloride above described. The two solutions were separated both in this and other experiments by an ordinary porous earthenware pot, and the E.M.F. was measured by balancing it against a difference of potential by Poggendorff's method.

The standards taken were a Latimer-Clark cell, which was assumed to have an E.M.F. of 1.435 volt at  $15^\circ C.$ , and a chloride of silver battery (modified De-la-Rue cell), which by comparison with the Clark cell was found to have an E.M.F. of 1.045 volt. I find this cell more convenient in using Poggendorff's, or any similar method, as its E.M.F. is not appreciably disturbed by its sending a small current, or by shaking, and it has a smaller temperature-coefficient than the Clark cell. The temperature of all the cells used in these experiments only varied between the narrow limits of from  $12^\circ$  to  $15^\circ C.$

In one experiment the zinc-platinum cell, when first set up, gave an E.M.F. of 1.647 volt. It was then allowed to send a current through a low external resistance for five minutes, and after further resting for five minutes its E.M.F. was again measured, when it was found to have dropped to 1.473 volt.

After a further rest of about ten minutes it recovered to 1.507 volt, at which value it remained tolerably constant. During the passage of the current from the cell the platinum plate became covered with a black deposit of finely divided platinum, and I thought it not improbable that this alteration of the surface might be the cause of the marked falling off in E.M.F.; but on removing the solution surrounding the platinum plate and replacing it with fresh, the E.M.F. regained its initial high value although the surface of the plate had not been disturbed. It appeared from this that the high initial value was probably due to oxygen dissolved in the liquid, which the platinum would be very apt to occlude superficially, and which would account for the uncertain values of the E.M.F.

Whatever may be the cause, this variability renders the measurement of the E.M.F. of this form of cell very difficult.

In other experiments values as high as 1.7 volt were obtained on first setting up the cell, which, after sending a current and resting, fell to the tolerably stable value of about 1.525.

Maximum E.M.F. = 1.70 volt.

Minimum „ = 1.473 „

Average „ 1.525 „

The average value (1.525) is seen to be slightly lower than the E.M.F. calculated from the thermochemical equation (1.548); but the difference is small (.023 volt), and is well within the limits of experimental error with such a variable cell. There is therefore no reason to assume that its actual E.M.F. departs from the theoretical value.

### *Zinc-Gold Cell.*

The heat of formation of  $[\text{Au}, \text{Cl}_3, \text{aq}]$  is given by Thomsen as 27,270 calories, and that of  $[\text{Zn}, \text{Cl}_2, \text{aq}]$  being 112,840, the difference per equivalent gives 2.044 volts as the theoretical E.M.F. of zinc, displacing gold from weak solutions of its chloride.

A cell consisting of an amalgamated zinc rod immersed in a solution of zinc chloride having the strength of .25ZnCl<sub>2</sub>.100H<sub>2</sub>O opposed to a plate of gold in a solution of auric chloride of equal molecular strength, was set up and its E.M.F. immediately measured. It was found to give an E.M.F. of 1.855 volt, and after actual short-circuiting for five minutes it had only fallen to 1.834. These values were in fact the extreme limits of the variations that I have observed on repeating the experiment, and the constancy of this cell

contrasts in a striking manner with the variability of the platinum cells.

Maximum E.M.F. = 1.855 volt.

Minimum       ,,       = 1.834       ,,

Mean       ,,       = 1.844       ,,

Assuming the thermal values for gold to be accurate, the actual E.M.F. thus measured is seen to be .2 volt below the calculated value; or, adopting the convention suggested by Messrs. Wright and Thompson,  $-0.2$  volt is the *thermo-voltaic constant* for gold in dilute neutral solutions of its chloride.

When a platinum plate was substituted for the gold plate and immersed in the gold-chloride solution, the E.M.F. of the cell thus formed was found to be 1.782 volt, *i. e.* less than the gold-gold chloride, but greater than the platinum-platinic chloride cell given above.

From the thermochemical values one might conclude that platinum would be capable of replacing gold from gold chloride; but, so far as my experiments have gone, I have not found this to be the case, nor on the other hand is gold able to replace platinum from platinic chloride, which, of course, is not to be expected.

When a plate of gold and another of platinum are immersed together in pure water or in dilute hydrochloric acid, the gold acquires slightly the higher potential. If strong hydrochloric acid be substituted for the dilute, the direction of the difference of potential becomes doubtful, and on the addition of nitric acid to the strong hydrochloric, so as to form *aqua regia*, the platinum acquires distinctly the higher potential, and if the outside circuit be closed on a galvanometer, a very decided current flows from the gold to the platinum through the cell (*cf.* Ganot's Physics, article on "Electromotive Series").

Why the nascent chlorine combines readily with the gold where it evolves but little heat and slowly and reluctantly with the platinum, in which reaction much more heat is disengaged, is a problem which at present appears to admit of no satisfactory solution.

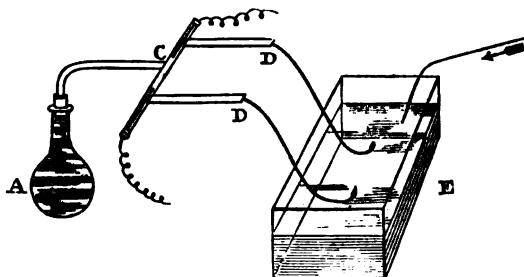


LX. *The Action of the Electric Discharge on Gases and Vapours.* By C. LUDWIG, Ph.D., Leipzig\*.

I HAVE during the past year made a number of experiments on the action of the electric discharge, as furnished by a Ruhmkorff coil, on gases and vapours of various substances for the purpose of establishing, if possible, whether or not electrolysis takes place.

There is a qualitative difference in the products of decomposition that collect at the poles, so far as experiment enables us to determine.

The apparatus that I used in the examination of water-vapour was suggested by Prof. E. Wiedemann, of Erlangen, and may be briefly described as follows:—



A flask, A, capable of holding nearly  $1\frac{1}{2}$  litres, is filled up to the neck with distilled water that has been boiled for 15 minutes immediately previous to the experiment. It is furnished with a singly perforated good cork, carrying a large tube of 8 millim. internal diameter, which serves to conduct the vapour from the flask into the sparking-tube, C; this tube is also 8 millim. in internal diameter. The two delivery-tubes passing from it are 60 millim. apart. The vapour coming from the flask A divides, in tube C, into two currents, which pass out by the delivery-tubes. The electrodes consist of copper wire  $3\frac{1}{4}$  millim. thick; they have flat polished ends, and are inserted into the tube C gas-tight by means of rubber stoppers, an arrangement that permits of their being set at various distances from one another. They are placed in such positions that they are located in currents of vapour travelling in opposite directions, as will be easily understood. By this means it is possible to ascertain whether or not there is a difference in the gases separated out at the poles, for these

\* Communicated by the Author.

may be collected and analysed. The entire sparking-tube is encased in an air-bath capable of being heated above  $100^{\circ}\text{C.}$ , and thus preventing any condensation. The delivery-tubes are firmly clamped and held in position with their ends exactly on the same level. This is effected by boiling the contents of the flask when only about three fourths full of water, and collecting the gases given off at once. If the tubes have their ends exactly on the same level, the volumes of gas delivered from each will be equal to one another. By repeated trial it is possible to accomplish this within limits entirely satisfactory. The water in the trough E is maintained at  $90^{\circ}\text{C.}$  or upwards by means of a current of steam, in order to reduce the error resulting from the different solubilities of oxygen and hydrogen as much as possible.

Each experiment lasted from three to four hours, during which time a constant current of steam was given off from the flask and was subjected to the action of the electric discharge, leaping over various intervals between the electrodes. As electromotive power, four Grove cells of Browning's make were used. The Ruhmkorff coil was used without condenser, and by its construction could give only a feeble extra current, because the section of the inducing wire was very large and its length very small in comparison with the induced wire. A Geissler tube inserted to remove the extra-current spark did not in any way alter the results obtained, thus substantiating my anticipations; consequently it was unnecessary to resort to the usual means of throwing out the extra-current spark.

When passing the spark at the beginning of an experiment, while there is still air in the apparatus, it is surprising to notice how, in proportion as this is expelled and the atmosphere becomes more and more one of pure vapour of water, the resistance to the passage of the spark increases. It would seem that, just as pure water is a very good insulator, so also pure water-vapour offers very great resistance: in fact it is possible to obtain sparks three times as long in air as in pure aqueous vapour.

At the conclusion of each experiment the gases were transferred to a eudiometer, and analysed in very much the same way as that used by Perrot (*Ann. de Chim. et de Phys.* vol. xli. p. 161, 1861). This savant conducted a great number of experiments on the electrolysis of aqueous vapour, extending his work over years of time.

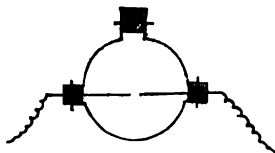
In the light of modern theories concerning the cause of electrolytic decomposition, as enunciated especially by Arrhenius, it seemed desirable that these experiments should be repeated.

Without entering into detail I think it will be only necessary to give the results of one of my experiments, which I consider very successful, and which differs from the rest only in better quantitative results, all being alike qualitatively.

In the experiment alluded to, after removal of the hydrogen and oxygen present in proportion necessary to form water, the residues were found to consist of excess of hydrogen—2.6 cubic centim. in the one tube, corresponding to the negative pole; and excess of oxygen, 1.7 cubic. centim. in the other, corresponding to the positive pole.

From the arrangement of the experiment it is clear that the temperatures of the electrodes must have been the same and constant, *i. e.* 100° C.

After having assured myself that the above differences in the products of decomposition of aqueous vapour by the electric discharge exist, I experimented next on hydriodic-acid gas, dried, and passed through the same apparatus. It was found that in this instance the decomposition took place very readily, and the positive pole became rapidly covered with iodine, while the negative pole presented a perfectly bright surface of copper. One of the products of decomposition being a solid it was not attempted, of course, to collect the gaseous product. On reversing the current, the poles remaining in the same position and having been previously cleaned, the same phenomenon was again observed, the iodine appearing only on the positive pole. The temperature of sparking was that of the room. But a few minutes were necessary to show the deposition of iodine. By this experiment, in fact, it is remarkably easy to show the distinctive action of the poles in decomposing vapours to a large audience. It is only necessary to fill a large flask having two tubulures, of the accompanying form, for example, to be found in any chemical laboratory, with dry hydriodic-acid vapour, and then to pass the discharge for, say, fifteen minutes. The electrodes may then be removed and passed round. The proof is thus convincingly furnished that vapours are capable of polar decomposition.



When the spark passes through the hydriodic-acid vapour, a great part of the decomposition is of course due to thermal dissociation, and a cloud of iodine vapour rises from between the electrodes at each discharge, rendering this phenomenon very apparent. It is hardly possible to separate perfectly the two modes of decomposition that evidently have place here, nor to understand how they exist side by side.

J. J. Thomson (Phil. Mag. [5] xxix. pp. 358 & 441, 1890) finds that hydriodic-acid vapour is an excellent conductor of electricity. He experimented by passing the vapours of his substances through a platinum tube heated to a yellow heat and having in it platinum electrodes. It is not impossible that we have here in part a true electrolytic decomposition, and that in amount it is in direct proportion to the conducting power.

A pure gas is, I think, not electrolytically decomposed on the passage of the first spark, and is practically a non-conductor. However, by the passage of the first spark there is produced by thermal dissociation a mixture of gases in the pathway of the discharge. This it is that conducts fairly well, so that then electrolysis may take place. The conduction of the current is therefore not simultaneous with the passage of the spark, and takes place only during a short time. Consequently the electrolytic and thermal dissociations are not simultaneous. The partial pressures of the substances electrolysed would thus be reduced, another factor in the promotion of electrolytic conduction.

This may be proved experimentally:—By taking a mixture of the original gas and its components it is possible to effect an electrolytic decomposition by means of the Ruhmkorff coil without the passage of any spark. Such a mixture was prepared, and the electrodes so adjusted that no spark could pass. Then what seems to be an electrolysis was effected, iodine being deposited on the positive pole. That this iodine was not free iodine of the mixture was proved by leaving it out entirely, and making instead a mixture of hydrochloric acid, hydriodic acid, and hydrogen. Then the same phenomenon was observed.

We are therefore justified in the conclusion, arrived at also by E. Wiedemann and J. J. Thomson, that the decomposition is in part a true electrolysis after the manner of a Grotthus chain. At least this is one interpretation we may give for the present.

We have therefore to do with an imperfect insulator, and the electrostatic energy is gradually transferred between the poles. It is necessary that the electromotive force should be sufficient to decompose the chemical compound, as otherwise no decomposition could have place, but only conduction. It would seem, further, that Thomson's view is correct—that the ease of decomposition of the molecule into atoms is proportional to the conducting power. In that gases at ordinary temperatures are such very poor conductors, it would seem that the conductivity is, as I stated above, the result of

dissociation by the discharge and the consequent diminution of pressure. I do not think, with Thomson, that the molecules cannot, while the atoms can conduct.

I think I have shown that while pure hydriodic-acid vapour does not conduct to any appreciable extent at ordinary temperatures when pure and dry, it does conduct when diluted with any diluent. Further, that electrolysis of vapours is only possible to any appreciable extent when the mechanical action of the spark has caused such dilution of the pure substance beforehand by dissociating it in part.

Further, I made an extended series of experiments on the action of the electric discharge on the following gases and vapours : viz. carbon tetrachloride, chloroform, carbon disulphide, silicon tetrafluoride, marsh-gas, olefiant gas, and coal-gas.

Where one of the products of decomposition is a solid, it is for obvious reasons not possible to use the apparatus above described to show a polar distribution of the products of decomposition. Now all these substances furnish solid deposits excepting silicon tetrafluoride, which was not decomposed.

The hydrocarbons yield deposits of carbon, and therefore it was impossible to find a difference in the gases furnished by our apparatus. However, a remarkable fact was observed, which I believe speaks strongly in favour of actual electrolysis, in the case of hydrocarbons especially. It is that the deposit of carbon for these latter always grew out from the positive pole in a way that would indicate its having been separated out at that pole and not mechanically projected against it. The experiment is most conveniently made with coal-gas, and the sparking done in a cylinder over mercury. The carbon grows from the positive pole in form of a very fine filament, very hard and very brittle, and possessing most excellent conducting power. The film is very thin, indeed thinner than a horse-hair. On examining it under the microscope it is found to be toothed in a very regular way, the teeth being sharp cones projecting towards the negative pole. The deposit could not possibly have been formed by mechanical projection of the carbon. From its character the carbon has not been carried to the pole and deposited there, but is, it seems to me, a true electrolytic separation. In any other way than this it would be difficult to explain the dendritic forms. Another thing that speaks against the mechanical projection supposition is that the filament is a mere slender thread. These forms have the greatest likeness to,

*Phil. Mag. S. 5. Vol. 33. No. 205. June 1892. 2 N*

and remind one very much of, the dendritic forms of metals that grow out from one pole in electrolysis of metallic solutions, and the current in that case seems to act just in the same way as in the gas.

Finally, when a slip of stiff writing-paper is placed between the two poles, one does not observe, on passing the discharge, a blackening of the side of the paper turned towards the negative pole, which would certainly be the case were the carbon deposited by projection on the positive pole.

There is, however, some carbon, in the form of soot that can be easily wiped off, deposited on the negative pole, though only in small amount. This deposit is entirely different from that on the positive pole both in quantity and quality, and I believe it is a true projection-deposit. Consequently the action of the electric discharge on this gas is not simple, but, as might be inferred, almost *à priori*, of complex character.

Firstly, and chiefly, we have an electrolytic decomposition by virtue of which the carbon is deposited in a well-conducting form on the positive pole; and, secondly, we have the dissociation due to the heat of the discharge alone, which in quantity is by far inferior to the former. By the heat of dissociation molecules of carbon are set free and are attracted by both the poles by virtue of their constant static charges.

Concerning the hydrocarbons examined—olefiant gas, marsh-gas, and coal-gas—there is no noticeable difference, qualitatively at least, in the action of the discharge, so that they need not be separately considered. The deposition of carbon takes place more rapidly in proportion as the gas contains a higher percentage of carbon; thus, under the same conditions in the same length of time, more carbon is deposited from olefiant gas than from marsh-gas.

The volumes of the two gases begin to increase rapidly at once on sparking, and very soon double the volume of the original is reached, so that the decomposition is no doubt perfect. This result seems anomalous, when we call to mind that acetylene is formed by the passage of the discharge between electrodes of carbon in an atmosphere of hydrogen. We are forced to the inevitable conclusion, which is rather interesting, that acetylene is not formed when only one of the electrodes is carbon, and that it is necessary that both the electrodes be carbon in order that it be formed.

Further, we must infer that it is very probable that acetylene is itself decomposed entirely when the two electrodes are metals or when only one of them is carbon.

The increment in volume when marsh-gas and olefiant gas

are subjected to the electric discharge is so rapid and striking that it can readily be demonstrated to a large audience in lecture.

The carbon separated out from each of these gases is the same in kind and form. Filaments 6 to 8 millim. long can be readily obtained in a few minutes, and on continuing the discharge they finally connect the two poles, when the spark ceases. The growth of the filament is entirely avoided by frequently reversing the current.

By the action of the electric discharge on vapour of chloroform no carbon filaments are formed, and chemically the decomposition is not simple in character. There is a large amount of gas formed consisting of chlorine (iodized starch-paper is blued) and hydrochloric acid (the gas is rapidly absorbed in part by water and the aqueous solution is strongly acid), while a dark red liquid is observed on the mercury of the eudiometer due to the solution of one of the products of decomposition in excess of the chloroform. A further examination of this was not attempted.

An exact measurement of the increment in volume of vapour was out of the question, owing to the action of the chlorine formed on the mercury of the eudiometer.

Carbon tetrachloride is decomposed very slowly indeed by the discharge. As in case of chloroform, so here also no carbon filament is formed, while the rate of decomposition is entirely different from that of chloroform. A voluminous yellow deposit is observed on the walls of the eudiometer around the negative pole and chlorine is set free, as appears by the starch test. The gaseous products of decomposition are not rapidly absorbed by water, as was the case with chloroform. A black deposit is observed on the surface of the mercury. Unquestionably, therefore, it follows from all this that the decomposition of carbon tetrachloride by the electric discharge is by no means simple in character.

When the electric discharge acts upon the vapour of carbon disulphide the volume diminishes rapidly. The vapour of this substance offers an enormous resistance to the passage of the discharge. When the poles are only 1 millim. apart only very few sparks pass through, the discharge taking its course outside round the eudiometer through the air, a distance twenty to thirty times as great, a proof that the vapour of carbon disulphide is an almost perfect insulator. In the course of the discharge a grey-blue smoke is observed which gradually pervades the entire volume of the vapour. Here, then, we have no noticeable evidence of electrolysis taking

place. The phenomenon seems to be a heat-dissociation pure and simple. There is deposited on both the poles, not the black conducting modification of carbon as in the case of marsh-gas &c., but a grey nonconducting matter around which the discharge leaps as it passes from wire to wire.

The appearance of the same character and quantity of deposit on each of the poles is, to my mind, conclusive evidence that we have to do here, not with an electrolysis, but with a heat-dissociation alone. I should make it a cardinal requirement for a phenomenon of this kind that the deposits on the poles be symmetrical and of equal amounts. By the heat-dissociation the molecules of carbon are liberated along the entire course of the discharge, and are, as the static charges of the poles are equal, attracted simply in one half of the field to the one pole and in the other half to the other pole.

The sulphur molecules liberated at the same time are, on account of the great heat, not deposited on the poles. Indeed in this decomposition, a yellow-brown mass is deposited on the sides of the tube which is nothing else than the sulphur condensed there.

Silicon tetrachloride does not appear to be acted on at all by the discharge. Attempts were made to electrolyse the haloid compounds of mercury in form of vapour. The results were all negative, which may, however, be owing to the great difficulties encountered in carrying out the experiments.

It would seem, finally, that some of the phenomena described are true electrolyses in part. Others seem to be "Thermolyses," that is, the compounds are simply dissociated by the heat of the discharge. The predilection of the atoms thus liberated for electricity of different kinds would make them, like pith-balls, fly to the pole having the charge opposite their own, and thus give the entire phenomenon the appearance in all respects of a true electrolysis, while in reality there is the greatest possible difference.

It is very difficult to separate the "Thermolysis" from electrolysis in the experiments I have described, and the phenomena indicate that in most cases described they go hand in hand

Washington University,  
St. Louis, March 1892.



LXI. *A Method for determining the Specific Inductive Capacity of Dielectrics.* By FREDERICK T. TROUTON, M.A., D.Sc., and W. E. LILLY, *Whitw. Exhib.\**

ON comparing the energy of a condenser charged with a certain quantity of electricity, first as a simple air-condenser, and secondly when a dielectric sheet of greater specific inductive capacity is introduced between the plates, we at once see that the energy in the second case is less than in the first; since the energy equals  $\frac{1}{2}QV$ , and  $V$  the difference in potential between the plates is less after the sheet is introduced than before,  $Q$  the quantity of electricity being the same in both cases.

In consequence, if a sheet of, say, sulphur be introduced between the plates of a charged condenser, it should be acted on by a force tending to suck it in between the plates. In short, the electric energy in the system being less after the introduction of the sulphur than before, work must have been done by the electric forces during the operation.

The first experiments made were directed towards proving this deduction from simple theory, and they conclusively showed that such a force existed.

The lines of force in a condenser run from one plate to the other, so that here the movement takes place at right angles to these lines of force. But it must be remembered that at the edge of the condenser the lines of force are curved outwards, more especially if a sheet of, say, sulphur is introduced there, and these, tending to contract, draw the sheet inwards.

The amount of this force depends on the specific inductive capacity of the dielectric of which the sheet is made, so that by observing the force we may determine this quantity for any given substance.

It is more convenient, in making experiments for this purpose, to keep the difference in potential of the plates constant by means of some source of electromotive force such as a storage battery, than to keep the charge constant; let  $V$  be this difference measured in electrostatic units. Then to find the force in terms of  $K$ , the specific inductive capacity of the sheet, suppose the sheet (fig. 1) to be withdrawn a certain distance  $x$ : the work done equals the energy pumped back to the battery through the consequent diminution of the charge of the condenser. Let  $E$ ,  $E_1$ , and  $E_1'$  be the energy, per cubic centimetre of the sheet, of the air between the plates, and of the air between the sheet and the plates; and if the thickness of the sheet be  $a$ , and the distance apart of the plates be  $(a+b)$ , then, provided the sheet is long, and well in between

\* Communicated by the Authors.

the plates so as to avoid changing all edge effects,

$$Fx = \{Ea + E_1'b - E_1(a+b)\} lx,$$

where  $l$  is the dimension of the sheet, supposed rectangular, perpendicular to the paper.

To find in terms of  $V$  and  $K$ , we have

$$E = \frac{K}{8\pi} f^2, \quad E_1 = \frac{K_1}{8\pi} f_1^2, \quad E_1' = \frac{K_1}{8\pi} f_1'^2,$$

and

$$fK = f_1K_1, \quad V = f_1(a+b) = fa + f_1'b,$$

where  $f$ ,  $f_1$ , and  $f_1'$  are the electric forces in the sheet, in the air between the plates, and in the air between the sheet and the plates,  $K_1$  being the specific inductive capacity of air.

$$\text{Then } F = \frac{V^2(K - K_1)al}{8\pi\left(a + \frac{K}{K_1}b\right)(a+b)}.$$

The form of apparatus we employed in our experiments had the condenser plates horizontal.

The dielectric sheet was formed into a double fan-shaped needle, and supported horizontally by a bifilar suspension. Two pairs of condenser-plates, as shown in fig. 2, were used so as to insure a torsional couple, the two upper and the two lower being for convenience connected together.

It is of course immaterial whether the upper plates are positive or negative, the deflexion always being in the same direction. In making the experiment the condenser-plates are connected up with a source of electricity, such as a battery of storage-cells, and the deflexion of the needle on coming to rest noted by means of a mirror and spot of light in the usual way. To find the torsional moment in terms of the electric quantities involved, the force on each element of edge area of the needle

Fig. 1.

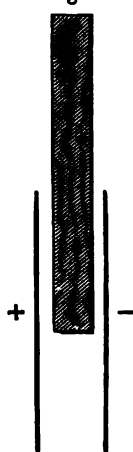
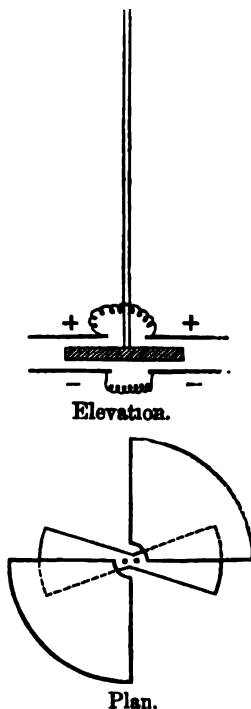


Fig. 2.



must be multiplied by its distance  $y$  from the centre, and summated between points situated approximately at the ends of the needle and at the inside edge of each condenser-plate.

$$T = 2 \int_0^{2l} \frac{V^2(K - K_1)a}{\left(a + \frac{K}{K_1}b\right)(a+b)} y dy,$$

where  $2l$  is the length of the needle, and  $2l'$  the diameter of the central opening for the bifilar suspension.

This is to be equated with  $Wg \frac{mn}{h} \sin \phi$ , the torsional moment of the bifilar suspension;  $W$  being the weight of the needle,  $g$  the acceleration of gravity,  $m$  and  $n$  the upper and lower distances apart of the threads,  $h$  their length, and  $\phi$  the angle turned through.

Thus the sine, or, if the deflexion is small, the angles turned through should be proportional to the square of the electromotive force applied to the plates. This was in complete agreement with our experiments on sulphur. Some experiments, however, made with a light ebonite needle gave angles of deflexion lying between the square law and a directly proportional law. This discrepancy was probably due to the unreliability of the bifilar method of suspension.

To calculate  $K$ , we have

$$K = K_1 \left( \frac{K_1 + Aa}{K_1 - Ab} \right), \text{ where } A = \frac{W \cdot g \cdot mn(a+b)\phi}{ha(l^2 - l'^2)V^2}.$$

The mean of several sets of experiments on sulphur gave the value  $K = 2.56$ ; but as our object was more to demonstrate the practicability of the method than to value  $K$ , we did not make arrangements for very accurately determining the quantities involved, and consequently we can put no great reliance on this number. Indeed, without a careful physical and chemical examination of the specimen of the substance under examination, a great degree of refinement is of little use, a fact too often lost sight of.

A considerable time-lag was always noticed on reversing the polarity of the condenser-plates. That is to say, the spot of light would go back towards zero a few divisions on reversing and then slowly creep up to the former value. It ultimately always came up to approximately the same value as before reversing, thus exhibiting little or no dielectric hysteresis.

By applying a rapidly alternating source of electromotive force to the condenser-plates an approximation towards the "instantaneous value" of  $K$  may thus be obtained. In fact the method is particularly suited to this purpose. Some

experiments made gave results varying from 2.33 to 2.47 ; but the alternator employed, being driven by an old type of gas-engine, ran very unevenly and rendered observations difficult.

In this case it is the average value of the square of the electromotive force which is required in calculating  $K$ , and this was obtained directly by employing a Cardew's voltmeter for determining the difference in potential of the plates.

One of the advantages in the method described in this paper is the possible avoidance (not realized, however, in the form used by us) of all doubtful approximate calculations. It is in this respect analogous to a method much advocated by Lord Kelvin for determining the magnetic permeability of iron.

When suitably modified for the necessary diminutive size, it appears also well adapted for such determinations as the specific inductive capacity of crystals in different directions.

We have much pleasure in thanking Prof. FitzGerald for his suggestions and help on many points which arose throughout our investigations.

LXII. *On the Difference of Potential at the Contact of Mutually Reacting Liquids.* By J. BROWN\*.

1. IN 1889 I began an investigation into the difference of potential at the contact of liquids, including aqueous solutions of electrolytes ; my object being to determine the connexion, if any, between this difference of potential and the chemical reaction of the liquids on one another. As circumstances may for some time prevent a return to this work, it seems well to make known what came of it, even though in a somewhat unfinished state.

The method employed was a modification of that of Exner and Tuma† in their experiments on the contact potential of metals and liquids, where the potential of a cylinder of filter-paper saturated with the liquid is ascertained by means of a funnel dropping mercury from a point in the interior of the cylinder. I used a water-dropping funnel as less likely to cause irregular indications by the action of gases on the issuing liquid, and as obviating the need of any correction for frictional electrification of the liquid at the nozzle. In the first apparatus employed, two cylinders or rolls of filter-paper were held in two short vertical glass tubes of about 2 centim. diameter mounted on paraffin insulators. These cylinders

\* Communicated by the Author.

† *Sitzungsberichte d. Kais. Akad. Wien*, xcvi. part ii. p. 1.

were saturated with the liquids to be tested, and contact between them was made either by a strip of the same paper, across which the two liquids soaked till they met, or by an arrangement consisting of two small funnels with fine drawn-out ends like those shown in fig. 2. These contained the two solutions connected by strips of filter-paper with their respective cylinders. As the liquids flowed out from the fine ends of the funnels they came in contact with continuously fresh surfaces, thus providing a continuous renovation of the surface of contact and preventing any possible permanent modification. I am not able to say, however, that this gives a result sensibly different from the simple paper connexion.

The water-dropping testing funnel was provided with a stopcock, and its nozzle had three fine jets. By means of an insulated adjustable support this nozzle could be placed at will in the interior of either paper cylinder. The water in it was connected to the electrometer-key by an immersed platinum plate. To make a test, the two cylinders A, B were prepared and connected as described above, and an earthed platinum strip was placed in contact with A. The funnel jet was then allowed to discharge in the interior of the cylinder A, and the difference of potential between its platinum connexion and that of A measured by deflexion on the Thomson electrometer. This deflexion of course includes measurement of any contact difference at platinum-liquid connexions. The funnel jet was then changed to B, and the deflexion again noted. The difference of these deflexions was taken as the contact difference of potential A/B of the two liquids.

2. The first few experiments made with this apparatus were based on the assumption that, as the oxidation of a metal by an electrolyte electrifies the metal negatively, the raising of a salt from a lower to a higher oxide or chloride might have the same effect. Strong solutions were used, but the exact strength was not ascertained.

TABLE I.

	Positive.	Negative.	E.M.F.
1.	Ferrous Sulphate .....	Hydrogen Peroxide .....	·07, ·07 volt.
2.	" .....	Potassium Permanganate...	·06, ·08 "
3.	" .....	Water + dissolved Oxygen .	·04 "
4.	" .....	Potassium Biochromate.....	·07 "
5.	Arsenious Acid .....	Iodine and Water.....	·10, ·12 "
6.	Stannous Chloride ...	Mercuric Chloride .....	·03 "
7.	Ferric Chloride.....	Sulphurous Acid .....	·07 "
8.	" .....	Hydrogen Sulphide .....	·20 "

In these well-known reactions the working hypothesis stated above is contradicted by all except No. 7. In No. 8, though chlorine is transferred from left to right, sulphur is eliminated from the hydrogen sulphide and there is thus a complicated reaction.

8. A number of experiments were now made in the hope of gaining some insight into the kind of results to be obtained from the contact of two solutions between which double decomposition occurred on mixing. After some trials of a tentative kind with solutions of unknown proportions which gave discordant and unsatisfactory results, the remainder were made with solutions containing equivalent proportions. At first the apparatus already described was used, and the numbers obtained with it will be found in column A, Table II. It did not, however, seem quite satisfactory, and I constructed another, which is represented diagrammatically in fig. 1 one ninth actual size. Two glass cylinders A, B, about 11 centim. long by 2 centim. diameter, were supported by holes in a paraffin bridge C by means of tight rubber bands *i*, *k*. The liquids to be tested were applied by means of pipettes to the interior of these cylinders, or to paper rolls supported

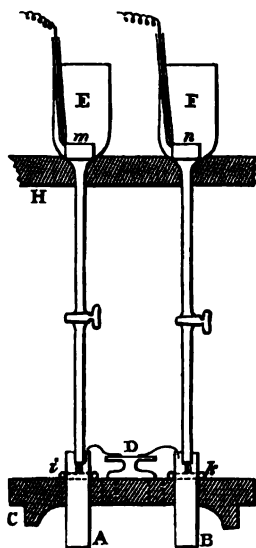


Fig. 1.



Fig. 2.

on shorter glass cylinders which were occasionally used instead of them. Contact was made between two little pools of the liquids on the top of the glass stand D, each connected to the liquid on its cylinder by a strip of filter paper, or, in the case of corrosive liquids, by a tuft of asbestos.

Sometimes this arrangement was replaced by a pair of funnels (fig. 2), as described above, carried in holes in the bridge C between the cylinders A, B. A second bridge H, also of paraffin, carried two triple-jet funnels E, F with stopcocks as shown. The water in each was connected to one terminal of the electrometer-key by means of wires enclosed in glass tubes and joined by platinum wires to the platinum plates *m, n*. The bridge H could be raised vertically upwards, sliding on the frame of the apparatus, so as to lift the jets clear of the cylinders, thus giving room for the supply of the solutions. This also provided for the reversal of the bridge C, which could be turned end for end; so that by taking the mean of observations in the two positions, any errors in the funnel part of the arrangement might be eliminated.

4. To make an experiment with this apparatus, the cylinders having been wetted with the given liquids, one being to earth, and contact between them having been established, the funnels were lowered into position, the stopcocks turned on so as to start the flow of the jets, and the deflexion read in the usual way by two reversals on the electrometer. The flow was then stopped, the funnels raised out of the way, the bridge C reversed, the funnels lowered, re-started, and a second reading taken. A third reading with the bridge C in the original position completed the observation, and the mean of the three readings was taken as the true difference of potential. The results obtained with this apparatus are given in column B, Table II. In this table the formulæ represent gramme-molecules; the affix Aq. represents 1 gramme of water. Column H contains the heat equivalent of the reaction according to Thomsen's data.

TABLE II.

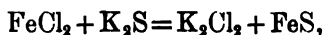
	Positive.		Negative.		H.		A.	B.
9.	FeCl <sub>2</sub>	250 Aq.	K <sub>2</sub> S	250 Aq.	12870	.....	-17	
10.	FeCl <sub>2</sub>	500 "	K <sub>2</sub> S	250 "	"	.....	.....	-11
11.	FeCl <sub>2</sub>	1000 "	K <sub>2</sub> S	1000 "	"	.....	.....	-18
12.	CdCl <sub>2</sub>	1000 "	K <sub>2</sub> S	1000 "	27150	{ Variable and reversing. }	.....	?
13.	CdCl <sub>2</sub>	1000 "	K <sub>2</sub> I <sub>2</sub>	1000 "	3920		-07	-06
14.	CdCl <sub>2</sub>	2000 "	K <sub>2</sub> I <sub>2</sub>	2000 "	"	.....	.....	-03
15.	HgCl <sub>2</sub>	6000 "	K <sub>2</sub> I <sub>2</sub>	6000 "	26750	.....	.....	-06?
16.	HgCl <sub>2</sub>	6000 "	K <sub>2</sub> S	6000 "	46070	.....	.....	-08
17.	HgCl <sub>2</sub>	6000 "	K <sub>2</sub> S	3000 "	"	.....	.....	-04
18.	PbCl <sub>2</sub>	4000 "	K <sub>2</sub> S	4000 "	33500	.....	-10	
19.	H <sub>2</sub> O <sub>2</sub>	7000 "	BaH <sub>2</sub> O <sub>2</sub>	7000 "	27780	.....	-07	-096
20.	H <sub>2</sub> O <sub>2</sub>	1000 "	Na <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1000 "	27490	.....	-003	
21.	CuCl <sub>2</sub>	1000 "	Na <sub>2</sub> H <sub>2</sub> O <sub>2</sub>	1000 "	12570	{ Variable and reversing. }	.....	-10?
22.	K <sub>2</sub> I <sub>2</sub>		I <sub>2</sub> Cl <sub>2</sub>		40640?		-20	

5. In the course of these experiments it became very evident that concordant and reliable results were difficult to obtain, partly on account of the smallness of the forces to be measured, and partly from a difficulty in ascertaining the exact origin of these forces so as to arrange the experiment in accord with them. Even the sign of the electrification sometimes reversed during the experiment, as in Nos. 12 and 21. The results must therefore be taken as only tentative, but in so far as they may be considered approximate they suggest the following conclusions:—

(i.) There is no clear connexion apparent between the observed electromotive forces and the heat equivalents of the reactions ; but the amount of water present seems to have an effect, either by the dilution of both solutions equally or one more than the other.

(ii.) The sign of the electrification may depend, however, on the following considerations. When double decomposition occurs at contact of solutions of two substances, one of which consists of an anion  $a$  and cation  $c$ , and the other of an anion  $a'$  and cation  $c'$ , the products of the reaction being  $ac'$  and  $a'c$ , then the solution  $ac$  will be positive if the combining heat  $a',c$  is greater than  $c',a$  ; and *vice versa*.

This hypothesis appears to conform to the following view of the kind of molecular action that may take place. In the case, for instance, of the reaction



the heat equivalent  $\text{K}_2\text{Cl}_2$  being greater than  $\text{FeS}$ , the molecules just before actually double-decomposing might be supposed to become polarized by the attraction between  $\text{K}_2$  and  $\text{Cl}_2$ , and so cause an electrification of the opposite ends of the system,



similar to that commonly associated with such a system as



Although this hypothesis receives support from nearly all the experiments in Table II., and also from several of the preliminary experiments not given in the table, it can scarcely be regarded as more than tentative, pending results of experiments under conditions of a more varied character.

6. In most of the numerous investigations already published dealing with contact potentials of liquids the potentials of the liquids were tested by means of a metallic connecting pole of platinum, mercury, or other such substance. The



electrolytic or voltaic effect of any action between the liquid and this immersed pole has been ignored, and an error of unknown amount has thus been introduced. There are, however, two series of experiments besides those of Exner and Tuma mentioned above in which this error has been avoided. In 1880 Ayrton and Perry\* described an apparatus for the investigation of the potential of liquids in contact, by their inductive action on plates of gilt brass held close above their surfaces. In 1883 Bichat and Blondlot† published an ingenious method involving the dropping of one of the liquids from a funnel whose jet was within a cylinder kept moistened by the other.

Partly from consideration of the large and striking character of the results obtained by these authors with strong acids, and partly in the search of a possible simplification of the problem, I have tested a series of pairs in which acids and strong aqueous solutions of various kinds were tried against water; the object being to ascertain whether the observed effects have any connexion with the heats of solution or dilution of these substances. The results are given in Table III., in which the first column contains the formulæ of the substances tested, with the water of solution, if any; the second column contains the results of the experiments, stated separately; and the third the heats of solution or dilution for the number of  $H_2O$  molecules stated, as given by Thomsen. The heats of dilution for potassium nitrate and chlorate are not available but are probably negative since the heats of solution of the anhydrous salts are negative.

A comparison between the numbers in the third and fourth columns shows that in the case of positive heats of solution there is a rough agreement between their amounts and those of the observed electromotive forces, while with negative heats the results appear variable and indefinite.

7. Table III. gives also a test of an hypothesis current among German physicists, which, premising that the ions are oppositely electrified, states that "water must show against every electrolytic solution the potential of the faster ion."

I have placed after each radical a number proportional to this "ionic velocity," according to F. Kohlrausch, as quoted in the Report of the British Association Electrolysis Committee for 1887‡. It appears that out of the fourteen pairs tried, in the four cases numbered 26, 27, 36, 37 water takes what would be assumed according to the above hypotheses as

\* Phil. Trans. 1880, p. 15.

† *Comptes Rendus*, xcvi. pp. 1202, 1293.

‡ B. A. Report (1887), pp. 338, 354.

TABLE III.

	Negative to Water.	Difference of Potential in Volts.	Heat equivalent.
23.	$\text{H}_2^{(272)}\text{SO}_4^{(40)}$ .....	1·58, 1·36, 1·40, 1·36.	17641 c. for 799 $\text{H}_2\text{O}$ .
24.	$\text{H}_2^{(272)}\text{N}_2\text{O}_6^{(48)}$ .....	1·02.	14986 " 640 "
25.	$\text{H}_2^{(272)}\text{Cl}_2^{(54)} + \text{about } 4\text{H}_2\text{O}$ ..	·79, ·63.	about 6300 " 300 "
26.	$\text{Zn}^{(24)}\text{Cl}_2^{(54)} + 5\text{H}_2\text{O}$ .....	·20, ·09, ·21.	8020 " 400 "
27.	$\text{Na}^{(32)}\text{N}_2\text{O}_6^{(48)} + 12\text{H}_2\text{O}$ ...	·08, ·02, ·22?	-4192 " 400 "
Positive to Water.			
28.	$\text{Na}_2^{(32)}\text{H}_2\text{O}_2^{(143)} + 6\text{H}_2\text{O}$ ...	·28, ·21.	5880 " 200 "
29.	" sat. solution .....	·19, diminishing.	
30.	$\text{K}_2^{(52)}\text{H}_2\text{O}_2^{(143)} + 6\text{H}_2\text{O}$ ...	·21, ·20.	5502 " 200 "
31.	$\text{Cu}^{(20)}\text{Cl}_2^{(54)} \text{ sat. solution}$ ...	·15, ·07.	4510 " 200 "
32.	$\text{Cu}^{(12)}\text{SO}_4^{(40)}$ " ...	·01.	
33.	" + $60\text{H}_2\text{O}$ .....	·03, ·03.	116 " 200 "
34.	$\text{Zn}^{(12)}\text{SO}_4^{(40)} + 20\text{H}_2\text{O}$ .....	·02, ·03.	390 " 200 "
35.	$\text{Na}_2^{(32)}\text{SO}_4^{(40)} + 50\text{H}_2\text{O}$ ...	·02, ·19.	-1383 " 400 "
36.	$\text{K}_2^{(52)}\text{N}_2\text{O}_6^{(48)}$ .....	Variable, small.	Probably negative.
37.	$\text{K}_2^{(52)}\text{C}_4\text{H}_4\text{O}_4^{(26)} + 10\text{H}_2\text{O}$ ..	·05, ·03.	3144 for 400 $\text{H}_2\text{O}$ .
Indifferent to Water.			
38.	$\text{K}_2^{(52)}\text{Cl}_2\text{O}_6^{(42)} \text{ sat. solution}$ ..	0.	Probably negative.

the potential of the slower "ion," and in No. 38 there is no sensible difference of potential accompanying the difference of ionic velocity indicated.

8. Besides these experiments on the contact potential of acids and water, the following three values were obtained between pairs of acids. They are of interest for comparison with the other results.

TABLE IV.

Positive.	Negative.	D.P. in Volts.
Nitric Acid .....	Hydrochloric Acid Solution	·30
Nitric Acid .....	Sulphuric Acid ..	·92
Hydrochloric Acid Solution	Sulphuric Acid .....	·62

I am indebted to Professor Everett for permission to carry out the above work in the Laboratory of Queen's College, Belfast, for suggestions regarding some of the methods employed, and for the use of the necessary apparatus.

### LXIII. *Proceedings of Learned Societies.*

#### GEOLOGICAL SOCIETY.

[Continued from p. 387.]

January 27, 1892.—Dr. W. T. Blandford, F.R.S., Vice-President, in the Chair.

THE following communications were read:—

1. "On the Hornblende-schists, Gneisses, and other Crystalline Rocks of Sark." By the Rev. Edwin Hill, M.A., F.G.S., and Prof. T. G. Bonney, D.Sc., F.R.S., V.P.G.S.

The authors refer to Mr. Hill's paper, published in 1887, for a general description of the Island. They were led to examine Sark again in the hope that its rocks might afford some clue to the genesis of the hornblende-schist of the Lizard. They describe the structure, macroscopic and microscopic, of the various foliated rocks. These are:—(a) The basement gneiss, a slightly foliated, somewhat granitoid rock, probably of igneous origin, but with some abnormal environment, and possibly intrusive into, instead of older than the rock which succeeds it. (b) The hornblende-schists, almost identical with those of the Lizard, but in one case yet more distinctly banded. (c) Banded gneisses sometimes rather fine-grained, variably banded: quartzofelspathic layers alternating with those rich in biotite or occasionally hornblende. Some of these gneisses resemble the "granulitic group" of the Lizard; others recall certain of the less coarse, well-banded gneisses of Scotland, *e. g.* south of Aberdeen. Sometimes they are much "gnarled" by subsequent earth-movements, by which, however, as a rule, the crystalline rocks of the Island do not appear to have been very seriously affected. (d) A very remarkable group of local occurrence which exhibits great variety. In some places large masses of a dark green hornblende-rock are broken up and traversed by a pale red vein-granite or aplite. The former rock is drawn out into irregular lenticles, elongated lumps, and finally streaks, and has been melted down locally into the aplite. This then becomes a well-banded biotite gneiss, which macroscopically and microscopically agrees with types which are common among the Archaean rocks. Sark therefore presents an example of the genesis of such a gneiss, and the authors are of opinion that probably all the above-named rocks are of igneous origin, but became solid ultimately under somewhat abnormal conditions, to which the peculiar structures (which distinguish them from ordinary igneous rocks) are due. They attribute the banding to the effect of fluxional movements, anterior to final consolidation,

in a mass to some extent heterogeneous. This hypothesis they consider may be applied to all gneisses or schists which exhibit similar structures—that is, to a considerable number (but by no means all) of the Archæan rocks.

The second part of the paper consists of notes on some of the dykes and obviously intrusive igneous rocks of the Island. Among these are four (new) dykes of “mica-trap,” one of which exhibits a very remarkable “pisolitic” structure. The variety of piorite described by Prof. Bonney in 1889 (from a boulder in Port du Moulin) has also been discovered *in situ*.

2. “On the Plutonic Rocks of Garabal Hill and Meall Breac.” By J. R. Dakyns, Esq., M.A., and J. J. H. Teall, Esq., M.A., F.R.S., F.G.S.

The plutonic rocks described occur in a complex forming a belt of high ground S.W. of Inverarnan. They vary considerably in composition, and though gradual passages are sometimes found between more or less acid rocks, at other times the junction is sharp. The more acid are always found to cut through the less acid when the two rocks are found in juxtaposition, and fragments occurring in a rock are less acid than the rock itself. Though thus shown to be of different ages, they must evidently be referred to one geological period. The first rocks to be formed were peridotites: then followed diorite, tonalite, granite, and eurite in order of increasing acidity.

The specific gravities, colours, and textures of the rocks are considered, and a detailed account of the constituent minerals given. The essential minerals are arranged in the following order, based on their general distribution in the different types of rock:—Olivine, pyroxene, hornblende, biotite, plagioclase, orthoclase and quartz, microcline. The following is the order in which the principal constituents commenced to form in the rocks:—Iron-ores, olivine, pyroxene, hornblende, biotite, plagioclase, orthoclase, microcline, and quartz. The chemical composition of the rocks is discussed, data being furnished by a series of analyses made by Mr. J. H. Player, and a diagrammatic representation of the molecular relations of the different bases and silica is given. The relations between mineralogical composition, chemical composition, and geological age are then considered; and the following conclusions are reached:—

- (1) That the various rocks have resulted from the differentiation of an originally homogeneous magma.
- (2) That the chronological sequence from peridotite to eurite is connected with the order of formation of minerals in igneous magmas.

3. “North Italian Bryozoa.—Part II. Cyclostomata.” By Arthur Wm. Waters, Esq., F.G.S.

LXIV. *Intelligence and Miscellaneous Articles.*

ON THE VALUE OF THE BRIGHTNESS OF SPECTRAL COLOURS WITH DIFFERENT ABSOLUTE INTENSITY. BY A. KÖNIG AND R. RITTER.

**J** PURKINJE was the first to point out that the relative brightness of different pigments was unequally influenced by a change in the intensity of their illuminations. In twilight blue is brighter than red, even though for mean illumination both colours seem to be equal. Dove and Seebeck subsequently pursued the phenomenon more minutely, and von Helmholtz found that it was also to be observed with spectral colours. If two differently coloured fields have the same brightness for mean illumination, then, after equal diminution in the objective intensity of both, that field which is illuminated by light of short wave-length will be the brighter, while after an increase of the intensity the longer wave-length seems brighter. Some years ago Brodhun \* investigated this "Purkinje's phenomenon" quantitatively, and found that with the illuminations he used it could no longer be observed at higher limits; that is to say, that beyond a certain illumination all colours alter their relative brightness to the same extent when their objective intensity is increased to the same extent. Only at this illumination are we entitled to represent by a curve the distribution of intensity in the spectrum without any special statement as to the illumination at which the comparisons are made. Brodhun has made and published such curves for my own eyes (normal trichromatic), for his own (green-blind), and for Ritter's (red-blind).

It is, however, apparent that curves of the distribution of brightness in the spectrum can be obtained for each degree of brightness; they possess then no value unless at the same time the degree of brightness is given in such a way that the curve can be reconstructed.

In a comprehensive research, of only a small portion of which I here give an account †, R. Ritter and I have endeavoured to obtain such curves for our own eyes, and for those of some other observers, at very different brightnesses. In the change of form of these curves with increasing absolute intensity, Purkinje's phenomenon must of course come out, so that with increasing brightness the ordinates increase the more, the longer is the wave-length of the spectrum-light in question; by this the maximum is displaced in the direction of the red end.

\* E. Brodhun, *Beiträge zur Farbenlehre*: Inaugural diss., Berlin 1887.

† A. König, "Ueber den Helligkeitswerth der Spectralfarben bei verschiedener absoluter Intensität." In *Beiträge zur Psychologie und Physiologie der Sinnesorgane*, von Helmholtz-Festschrift: Hamburg and Leipzig, 1891 (Leopold Voss).

The observation was made so that a surface which contained light of the wave-length  $535\ \mu\mu$  (thallium green) was always kept unaltered, and then the quantity of light expressed in breadths of the slit was determined which was necessary to attain the same brightness with the various wave-lengths of the spectrum in question. The reciprocal of this breadth of slit I call the value of the brightness of the spectral light examined for the given illumination.

The lowest degree of illumination was very near the lower limit of excitation, it was so feeble that the observer had to be at least a quarter of an hour in absolute darkness to perceive it at all. If we call the quantity of light 1, which was necessary to produce this brightness in the standard green field, the other shades of brightness used are given by the quantities of light 16, 256, 1024, 4096, 16384, 65536, and 262144. The last degree corresponds about for my eye to the illumination under which a white paper, lighted with 600 candles at a distance of a metre, appears when I view it through a diaphragm of 19 millim. aperture.

The principal results obtained by the various observers may be summed up in the following statements, in which all data refer to the dispersion spectrum of gas-light:—

1. For all observers (two trichromatic, a green-blind, and a red-blind) the curve for the values of brightness had almost exactly the same form for the darkest shade, and it was that which has been observed by Donders, Hering, Dieterici, and myself for greater shades of brightness in congenital monochromasy. Its maximum was at about  $535\ \mu\mu$ .

2. As the brightness increases the maximum increases with trichromatic persons, at first slowly, then more rapidly, and at length very slowly again. In the highest shade used it is about  $610\ \mu\mu$ .

3. So far as the observations extend, green-blind persons exhibit the same phenomena as the trichromates.

4. With red-blind persons the maximum moves at first towards the long wave-length, but with mean illumination attains the wave-length  $570\ \mu\mu$ , and remains here stationary for higher shades also, so far as the observations extend.

The statement in (1) was foreseen by Mr. E. Hering and the adherents of his theory, and was also observed shortly before the publication of our investigations. But that we are not justified in seeing in it a proof of the correctness of this theory follows from the observation, also made simultaneously by myself, that the distribution of brightness in the spectrum in individual cases is also unchanged, when by certain pathological processes the real sensation of colour is completely lost and only the sensation black-grey-white remains.—Wiedemann's *Annalen*, No. 3, 1892.

ON THE GLOW-DISCHARGE. BY E. WARBURG.

The results of the present investigation are thus summarized by the author:—

1. The electrostatic attraction which a plane cathode surface experiences in the glow-discharge can be measured by the balance, and from it the electrical force and the surface-density on the cathode surface can be determined. That attraction is proportional to the density of the current, and for bright platinum and aluminium electrodes amounts, in milligrammes per ampere, in

Dry nitrogen . . . . .	from 0.5 to 2 mm. pressure,	1300–2400.
Slightly moist nitrogen . .	” ” ”	500–800.
Hydrogen . . . . .	from 1–3 mm. pressure,	200–350.

2. In the negative glow-light there is, as A. Schuster has pointed out\*, an excess of free positive electricity. The amount of this positive charge is opposite and equal to the negative charge of the cathode. Like this charge it is proportional to the square root of the density of the current, and has been found to amount to about  $10^{-10}$  coulomb sq. cm. for 1 milliampere per square centimetre with bright platinum and aluminium cathodes in nitrogen and hydrogen.

3. The surface of an anode is much more feebly attracted, and is therefore much more feebly charged than the surface of a cathode.

If, then, two infinitely large parallel electrode surfaces are opposite each other, they are equally strongly charged only so long as the electricity is in equilibrium. If, however, the glow-discharge passes between the surfaces, the charge of the anode is feebler than the charge of the cathode by the excess of free positive electricity which is present in the gas through which the current passes.

4. At the normal density at which the negative glow-light can spread freely over the cathode, the electrical force at the cathode decreases with decrease of pressure, and is less for hydrogen than for nitrogen, in accordance with the laws of the striking-distance. At normal density, therefore, the excess of free positive electricity in the gas, mentioned under 3, decreases with decrease of pressure.

5. The material electrical charge of the gas which takes place in the glow-discharge brings with it an increase of the hydrostatic pressure, and therefore under ordinary circumstances produces eddy currents, which flow between limited electrodes from the anode to the cathode, and may account for the so frequently observed transfer of matter in the direction of the positive current.—Wiedemann's *Annalen*, No. 1, 1892.

\* Proc. Roy. Soc. vol. xlvii. p. 541 (1890).

PRIZE FOR RESEARCHES IN PHYSICS,  
OFFERED BY SCHNYDER VON WARTENSEE'S FOUNDATION  
FOR SCIENCE AND ART, ZÜRICH.

For the year 1894 a prize is offered by "Schnyder von Wartensee's Foundation," for the solution of the following problems in the domain of Physics:—

"As the numbers which represent the atomic heats of the elements still show very considerable divergences, the researches conducted by Professor H. F. Weber on boron, silicium, and carbon, regarding the dependence of the specific heats upon the temperature, are to be extended to several other elements, prepared as pure as possible, and also to combinations or alloys of them. Further, the densities and the thermic coefficients of expansion of the substances investigated are to be ascertained as carefully as possible."

The conditions are as follows:—

*Art. I.* The treatises handed in by competitors for the prizes may be in German, French, or English, and must be sent in by September 30, 1894, at the latest, to the address given in *Art. VI.*

*Art. II.* The examination of the treatises will be entrusted to a committee consisting of the following gentlemen:—

Professor Pernet, Zürich.

Professor A. Hantzsch, Zürich.

Professor E. Dorn, Halle-on-the-Saale.

Professor J. Wislicenus, Leipsic.

Professor E. Schär, Zürich, as member of the committee offering the prizes.

*Art. III.* The Prize Committee is empowered to award a first prize of Two Thousand Francs, and minor prizes at its discretion to the amount of One Thousand Francs.

*Art. IV.* The work to which the first prize is awarded is to be the property of Schnyder von Wartensee's Foundation, and arrangements will be made with the author regarding its publication.

*Art. V.* Every treatise sent in must have a motto on the title-page, and be accompanied with a sealed envelope bearing the same motto outside and containing the author's name.

*Art. VI.* The treatises are to be sent in to the following address within the period named in *Art. I.*:—

"An das Praesidium des Conventes der Stadtbibliothek Zürich"  
(betreffend Preisaufgabe der Stiftung von Schnyder von  
Wartensee für das Jahr 1894).

Zürich, December 31, 1891.



## INDEX TO VOL. XXXIII.

- A**BSORPTION-spectra of some copper salts, on the, 317.
- Adler (G.) on a consequence of the Poisson-Mossotti theory, 233.
- Air-cavities and flaws, on the influence of, on the strength of materials, 70.
- Anderson (Prof. A.) on the resistance and self-induction of branched circuits, 352.
- Ångström (K.) on the intensity of the radiation of gas under the electrical discharge, 387.
- Arons (L.) on an electrolytic experiment, 395.
- Ayrton (Prof. W. E.) on the construction of non-inductive resistances, 186.
- Baily (W.) on the construction of a colour map, 496.
- Barus (C.) on the change of heat conductivity on passing isothermally from solid to liquid, 431.
- Beams, on the resistances to transverse strain in, 397.
- Blake (Rev. J. F.) on the Cambrian rocks in Caernarvonshire, 384.
- Boltzmann's theorem, on Maxwell's investigation respecting, 356.
- Bonney (Prof. T. G.) on the euphotide or saussurite-samaragdite gabbro of the Saasthal, 237; on the crystalline rocks of Sark, 539.
- Books, new:—Ostwald's Solutions, 144; Watts's Index of Spectra: Appendix B, 147, Appendix C, 475; Gore's Star Groups, 147; Williamson's Integral Calculus, 148; Besant's Solutions of Examples in Conic Sections, 149; Parker's Elementary Thermodynamics, 228; Maxwell's Theory of Heat, 231; Blake's Annals of British Geology, 314; Karrer's Guide through the Collection of Building-materials in the Imperial Natural-History Museum at Vienna, 382; Worthington's Dynamics of Rotation, 383.
- Brown (J.) on the theory of electrolytic conduction of Clausius, and the dissociation theory of electrolysis, 82; on the difference of potential at the contact of mutually reacting liquids, 532.
- Burton (Dr. C. V.) on the constitution of matter, 191.
- Calc-spar, on the selective absorption of light in, 379.
- Callendar (H. L.), experiments with a platinum pyrometer on the melting-points of gold and silver, 220.
- Cambrian rocks in Caernarvonshire, on the, 384.
- Chemical union &c., on the loss of energy due to, 28.
- Circuits, on the resistance and self-induction of branched, 352.
- Cohen (R.) on the influence of pressure on the viscosity of liquids, 476.
- Coils, on the calculation of the induction-coefficients of, 62; on choking, 433.
- Colour map, on the construction of a, 496.
- Colours, on the brightness of spectral, with different intensity, 541.
- Constants, on the determination of critical, 181.
- Copper salts, on the absorption-spectra of some, 317.
- Crew (H.) on a new method for obtaining a constant temperature, 89.
- Curvature, on the recognition of changes of, by means of a flexible lath, 436.
- Dakyns (J. R.) on the plutonic rocks of Garabal Hill, 540.
- Dielectrics, on a method for determining the specific inductive capacity of, 529.
- Diffusion of gases, calculation of probability respecting, 296.
- Electric discharge, on the action of the, on gases and vapours, 521.
- Electrodynamometers, on absolute, 69.

- Electrolysis, on the dissociation theory of, 82.  
 Electrolytes, on chemical equilibrium in mixed, 342.  
 Electrolytic conduction, on Clausius's theory of, 82.  
 — experiment, an, 395.  
 Electromagnetic radiation, on a method of determining, 396.  
 Electromotive force of gas-batteries, on the, 235; of gold and of platinum cells, on the, 516.  
 Energy, on the loss of, due to chemical union &c., 28; on the kinetic theory of the dissipation of, 291; on the Maxwell-Boltzmann doctrine regarding distribution of kinetic, 466.  
 Euphotide of the Saasthal, on the, 237.  
 Ewan (Dr. T.) on the absorption-spectra of some copper salts in aqueous solution, 317.  
 FitzGerald (M. F.) on the flexure of long pillars under their own weight, 428.  
 Flaws and air-cavities, on the influence of, on the strength of materials, 70.  
 Flexure of long pillars under their own weight, on the, 428.  
 Formulæ, on arithmetical recurring, 54.  
 Garrett (T. A.) on a detector for spark in Hertz's resonator, 290.  
 Gas, on the intensity of the radiation of, under the influence of the electrical discharge, 387.  
 Gas-batteries, on the electromotive force of, 235.  
 Gases, calculation of probability respecting diffusion of, 296; on the action of the electric discharge on, 521.  
 Geological Society, proceedings of the, 149, 384, 539.  
 Glaisher (Dr. W. J. L.) on arithmetical recurring formulæ, 54.  
 Glass, on the selective absorption of light in, 379.  
 Glen Roy, remarks on, 149.  
 Glow-discharge, on the, 543.  
 Gold and tin, on the existence of a compound of, 94.  
 —, on the melting-point of, 220.  
 Gold cells, on the electromotive force of, 516.  
 Gore (Dr. G.) on the loss of energy due to chemical union &c., 28; on chemical equilibrium in mixed electrolytes, 342.  
 Gray (Prof. A.) on the calculation of the induction-coefficients of coils, and the construction of standards of inductance, and on absolute electro-dynamometers, 62.  
 H, on a galvanometric method of measuring, 78.  
 Harrison (Prof. J. B.) on the geology of Barbados, 386.  
 Heat conductivity, on the change of, on passing isothermally from solid to liquid, 431.  
 Herroun (Prof. E. F.) on the electromotive forces of gold and of platinum cells, 516.  
 Hertz's resonator, on a detector for spark in, 290.  
 Hesehus (N.) on the refraction of sound and its velocity in porous substances permeable to sound, 316.  
 Hibbert (W.) on a permanent magnetic field, 307.  
 Hill (Rev. E.) on the crystalline Rocks of Sark, 539.  
 Hughes (R. E.) on some properties of dried hydrogen sulphide gas, 471.  
 Hull (Prof. E.) on the red rocks of the S. Devon Coast, 161.  
 Hydrogen sulphide gas, on some properties of dried, 471.  
 Inductance, on the construction of standards of, 62.  
 Induction-coefficients of coils, on the calculation of the, 62.  
 Irving (Rev. A.) on the red rocks of S. Devon, 151.  
 Isothermal formula, on a dynamical illustration of the, 301.  
 Jamieson (T. F.), remarks on Glen Roy, 149.  
 Jukes-Browne (A. J.) on the geology of Barbados, 386.  
 Kelvin (Lord) on the kinetic theory of the dissipation of energy, 291; on a decisive test-case disproving the Maxwell-Boltzmann doctrine regarding distribution of kinetic energy, 466.  
 Klemenčič (Prof.) on a method of determining electromagnetic radiation, 396.  
 König (A.) on the brightness of spectral colours with different intensity, 541.  
 Larmor (J.) on the influence of flaw

- and air-cavities on the strength of materials, 70.
- Laurie (A. P.) on the existence of a compound of gold and tin, 94.
- Lebedew (P.) on the repulsive force of radiating bodies, 391.
- Lehfeldt (R. A.) on a galvanometric method of measuring  $H$ , 78.
- Light emitted from incandescent zinc oxide, on the, 19; on the selective absorption of, by optical glass and calc-spar, 379.
- Lilly (W. E.) on a method for determining the specific inductive capacity of dielectrics, 529.
- Liquid surfaces, on reflexion from, in the neighbourhood of the polarizing angle, 1.
- Liquids, on the concordance of orthobaric curves for solutions and homogeneous, 152; on the influence of pressure on the viscosity of, 476; on the difference of potential at the contact of mutually reacting, 532.
- Love (A. E. H.) on the influence of a spherical cavity on the strength of materials, 76.
- Lucas (W.) on a detector for spark in Hertz's resonator, 299.
- Ludeking (Dr. C.) on the action of the electric discharge on gases and vapours, 521.
- McAulay (A.) on quaternions as a practical instrument of physical research, 477.
- McCowan (J.) on the solitary wave, 236; on the theory of long waves, 250.
- Magnetic field, on a permanent, 307.
- Magnetism, on the wave propagation of, 374.
- Manganese, on the hypothetical tetrachloride of, 284.
- Markovsky (G.) on the electromotive force of gas-batteries, 235.
- Mather (T.) on the construction of non-inductive resistances, 186.
- Matter, on the constitution of, 191.
- Maxwell's investigation respecting Boltzmann's theorem, 356.
- Melde (F.) on the velocity of sound in membranous bodies, 236.
- Mendeléeff (Prof. D.) on the variation in the density of water with the temperature, 99.
- Monckton (H. W.) on the gravels on the south of the Thames, 385; on the Bagshot beds, 386.
- Natanson (Dr. L.) on the concordance of orthobaric curves of solutions and homogeneous liquids, 152; on a dynamical illustration of the isothermal formula, 301.
- Nichols (E. L.) on the light emitted by incandescent zinc oxide, 19; on the selective absorption of light by optical glass and calc-spar, 379.
- Nichols (R. C.) on the resistances to transverse strain in beams, 397.
- Nicholson (A. C.) on high-level glacial gravels near Oswestry, 385.
- Perry (Prof. J.) on struts and tie-rods with lateral loads, 269; on choking coils, 433.
- Pickering (S. U.) on the densities of sulphuric-acid solutions, 132, 403; on the hypothetical tetrachloride of manganese, 284; on the recognition of changes of curvature by means of a flexible lath, 436.
- Platinum cells, on the electromotive force of, 516.
- Poisson-Mossotti theory, on a consequence of the, 233.
- Potential, on the difference of, at the contact of mutually reacting liquids, 532.
- Pressures, temperatures, and volumes, on "corresponding," 153.
- Pyrometer, experiments with a platinum, on the melting-points of gold and silver, 220.
- Quaternions as a practical instrument of physical research, on, 477.
- Radiating bodies, on the repulsive force of, 391.
- Radiation of gas under the influence of the electrical discharge, on the, 387.
- , on a method of determining electromagnetic, 396.
- Rayleigh (Lord) on reflexion from liquid surfaces in the neighbourhood of the polarizing angle, 1; on the theory of surface-forces, 209, 468; on Maxwell's investigation respecting Boltzmann's theorem, 356; experiments on surface-films, 363.
- Recurring formulae, on arithmetical, 54.
- Reflexion from liquid surfaces in the neighbourhood of the polarizing angle, on, 1.
- Refraction of sound, on the, 816.

- Resistance of branched circuits, on the, 352.
- Resistances, on the construction of non-inductive, 186.
- Resonator, on a detector for spark in Hertz's, 299.
- Ritter (R.) on the brightness of spectral colours with different intensity, 541.
- Rocking-stones, on the formation of, 359.
- Rücker (Prof. A. W.) on the density and composition of dilute sulphuric-acid, 204.
- Saussurite-smaragdite gabbro of the Saasthal, on the, 237.
- Schnyder von Wartensee Prize for researches in physics, 544.
- Self-induction of branched circuits, on the, 352.
- Shone (W.) on the subterranean denudation of the glacial drift, 384.
- Silver, on the melting-point of, 220.
- Snow (B. W.) on the light emitted by incandescent zinc oxide, 19; on the selective absorption of light by optical glass and calc-spar, 379.
- Sodium, analysis of the spectrum of, 503.
- Solutions and homogeneous liquids, on the concordance of orthobaric curves for, 152.
- Sound, on the velocity of, in membranous bodies, 236; on the refraction and velocity of, 316.
- Spectra of some copper salts, on the absorption-, 317.
- Stoney (Dr. G. J.) on the analysis of the spectrum of sodium, 503.
- Strain in beams, on the resistances to transverse, 397.
- Struts and tie-rods with lateral rods, on, 269.
- Sulphuric-acid solutions, on the densities of, 132, 204, 463.
- Surface films, experiments upon, 363.
- , forces, the theory of, 209.
- Teall (J. J. H.) on the plutonic rocks of Garabal Hill, 540.
- Telescope, on the intensity at the focal point of a, when the object-glass is covered by a diaphragm pierced with circular apertures, 266.
- Temperature, on a new method for obtaining a constant, 89; on the variation in the density of water with the, 99.
- Temperatures, pressures, and volumes, on "corresponding," 153.
- Thomson (Sir W.) see Kelvin (Lord).
- Tides in rivers and estuaries, on the theory of, 261.
- Tie-rods, on struts and, with lateral loads, 269.
- Tin, on the existence of a compound of gold and, 94.
- Tomlinson (C.) on the formation of rocking-stones, 359.
- Trouton (Dr. F. T.) on a method for determining the specific inductive capacity of dielectrics, 529.
- Trowbridge (J.) on the wave propagation of magnetism, 374.
- Van der Waals's generalizations regarding "corresponding" temperatures, pressures, and volumes, on, 153.
- Vapours, on the action of the electric discharge on, 521.
- Viscosity of liquids, on the influence of pressure on the, 476.
- Walker (J.) on the intensity at the focal point of a telescope when the object-glass is covered by a diaphragm pierced with circular apertures, 266.
- Warburg (E.) on the glow-discharge, 543.
- Water, on the variation in the density of, with the temperature, 99.
- Wave propagation of magnetism, on the, 374.
- Wave, on the solitary, 236.
- Waves, on the theory of long, 250.
- Young (Dr. S.) on the generalizations of Van der Waals regarding "corresponding" temperatures, pressures, and volumes, 153.
- Zinc oxide, on the light emitted by incandescent, 19.

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# CONTENTS OF N° 205.—*Fifth Series.*

---

LVI. Quaternions as a practical Instrument of Physical Research. By ALEXANDER M <sup>c</sup> AULAY, M.A., Ormond College, Melbourne .....	page 477
LVII. On the Construction of a Colour Map. By WALTER BAILY, M.A. (Plate VIII.) .....	496
LVIII. Analysis of the Spectrum of Sodium, including an Inquiry into the true place of the Lines that have been regarded as Satellites. By G. JOHNSTONE STONEY, M.A., D.Sc., F.R.S., Vice-President, Royal Dublin Society. (Plates VI. & VII.) .....	503
LIX. A Note on the Electromotive Forces of Gold and of Platinum Cells. By E. F. HERROUN, Professor of Natural Philosophy in Queen's College, London.....	516
LX. The Action of the Electric Discharge on Gases and Vapours. By C. LUDEKING, Ph.D., Leipsic.....	521
LXI. A Method for determining the Specific Inductive Capacity of Dielectrics. By FREDERICK T. TROUTON, M.A., D.Sc., and W. E. LILLY, Whitw. Exhib.....	529
LXII. On the Difference of Potential at the Contact of Mutually Reacting Liquids. By J. BROWN.....	532
LXIII. Proceedings of Learned Societies :—	
GEOLOGICAL SOCIETY :—Rev. E. HILL and Prof. T. G. BONNEY on the Hornblende-schists, Gneisses, and other Crystalline Rocks of Sark ; Messrs. J. R. DAKYNS and J. J. H. TRALL on the Plutonic Rocks of Garabal Hill and Meall Breac ..	539, 540
LXIV. Intelligence and Miscellaneous Articles :—	
On the Value of the Brightness of Spectral Colours with different absolute Intensity, by A. König and R. Ritter....	541
On the Glow-Discharge, by E. Warburg .....	543
Prize for Researches in Physics, offered by Schnyder von Wartensee's Foundation for Science and Art, Zürich .....	544
Index .....	545
With Titlepage, Contents, &c.	

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